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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: 9/16/74

Project Title: Identification and Quantification of Organic Contaminants from Textile Processing

Project No: E-27-626

Principal Investigator: Dr. Wayne C. Tincher

Sponsor: Dept. of Natural Resources, Environmental Protection Division

Agreement Period: From 7/1/74 Until 6/30/75

Type Agreement: Contract dated 7/1/74

Amount:

$20,880	EPD
5,000	GIT (E-27-312)
$25,880	Total

Reports Required:

Monthly Progress Reports
Final Technical Report

Sponsor Contact Person (s):

Mr. F. Steve Ivey
Management Analyst
Department of Natural Resources
Environmental Protection Division
47 Trinity Avenue
Atlanta, Georgia 30334

Assigned to: Textile Engineering

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- Other

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GEORGIA INSTITUTE OF TECHNOLOGY
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RESEARCH PROJECT TERMINATION

Date: February 11, 1976

Project Title: Identification & Quantification of Organic Contaminants from Textile Processing

Project No: E-27-626

Principal Investigator: Dr. W. C. Tincher

Sponsor: Dept. of Natural Resources, Environmental Protection Division

Effective Termination Date: 8/31/75

Clearance of Accounting Charges: 9/30/75

Grant/Contract Closeout Actions Remaining: Final Invoice (FHH)

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File: E-27-626

Monthly Progress Report Number 1

(August 1 - August 30, 1974)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division

Department of Natural Resources

State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher

School of Textile Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

I. Introduction

The Textile and allied industries are the largest component of the industrial base of the state of Georgia. Manufacture of carpets and rugs is a major segment of this industry and this segment is highly concentrated in the Coosa River Basin. This industry uses and discharges large volumes of organic contaminants (dyes, surfactants, auxiliaries, finishes) to the Coosa River and it tributaries. The identities and quantities of many of these materials being discharged to streams is not known and assessment of possible adverse effects on biological systems is not possible. This problem is especially acute in the Coosa Basin since streams receiving textile wastes are water supply sources for a number of cities and towns.

This research project is directed toward determining the nature and quantities of organic material discharged by the carpet and rug industry. The work is divided into three phases with the following objectives:

I. Determine the types and quantities of organic compounds used and discharged by the carpet industry.

II. Develop analytical techniques for materials discharged in large volumes or chemicals which are probable health hazards.

III. Determine actual concentrations of compounds selected for study in II above by analyses of samples taken from the Coosa River Basin.

Major effort during the early stages of the project will be directed toward

the first objective. The major result of this effort will be a table listing the chemicals used in carpet production, the poundage consumed in 1974, the predicted consumption in 1980, the per cent that remains in the product and the per cent discharged to air, water, and solid waste.

II. Organization of the Study

The particular chemicals used in production of carpets will be directly related to the type of fiber in the face yarn. The first major division can therefore be made by face yarn type. The fibers currently being used in carpet production are shown in Table 1. The volume consumed in 1973 and the predicted consumption in 1978 are also shown (Reference 1). Four different processes are used for coloration of carpet face yarn-yarn dyeing, beck dyeing, continuous dyeing and printing. The face yarns that are processed by each of the methods is indicated by an X in Table 1. For any given type yarn dyed in a given process, there will be little variation from manufacturer to manufacturer in the process or the kinds of chemicals used. If the quantities of each type of fiber processed by each method can be determined, a good estimate of the quantities of chemicals used can be obtained. Process technology and chemical physical properties can then be employed to estimate quantities of chemicals in waste streams, in air, in solid wastes and in the product.

A list of the types of materials used in the dyeing processes and likely to be a part of carpet mill waste are shown in Table 2. Each type of material will not be used in every process. For example, thickeners are used in printing but not in yarn, beck , or continuous dyeing. The materials listed in the

"Other" category are not added to the dye beck by the carpet manufacturer but are materials which are present on the fiber processed into carpet. These materials are added by the fiber manufacturer and are either partially or completly removed in the carpet dye bath. They must therefore be considered as part of the total waste from carpet manufacturing.

Materials used in the finishing of carpets are shown in Table 3. Two methods of carpet backing are used - latex with a jute secondary and attached foam. The per cent of carpet finished by each of these two processes should give a good estimate of the quantities of materials used.

III. Information Sources

Four main sources of information are being searched as part of this study. The technical literature published in professional and trade journals contains a number of articles describing processes, techniques, and materials for dyeing and finishing of carpets. In addition, all fiber manufacturers issue technical bulletins describing typical processes for dyeing and finishing of carpets produced from their fibers. Similar bulletins are prepared by some chemical supply houses. These recommended procedures are widely accepted by carpet manufacturers with usually only minor modifications. At various times the industry compiles data and issues reports on projected markets for various types and styles of carpets or on major changes in process technology (i.e. printing or continous dyeing). These reports are usually issued by trade associations (Carpet and Rug Institute, American Dye Manufacturers Institute, etc.) and will be useful in determining quantities of fibers processed by various techniques.

These published sources will be supplemented by data supplied by personal contacts within the industry. Several contacts in carpet manufacturing firms and with key suppliers to the industry have agreed to cooperate in this study.

In some cases the available literature will have to be augmented by data collected in laboratory experiments.

IV. Present Status of the Research

The major effort to the present time has been directed toward determining the principal dyes used in carpet processing. The bulletins and technical articles in references 2-13 have provided the initial list of 115 dyes used in carpet processing. Of these, the 38 with known structures are listed in Tables 4, 5, and 6. Chemical structures are given in Appendix A.

Since nylon fiber now accounts for approximately 70% of carpet face yarn processed, the dyes shown in Table 4 are used in much larger volumes than those shown in Tables 5 and 6. Attempts are now underway to define more clearly the dyes that are used in largest volume.

Preliminary work has also been done on the composition of dye baths and printing pastes used in the carpet industry. A preliminary report on some of the more important auxiliaries used in dyeing will be included next month.

V. Technical Review Meeting

A meeting to reveiw the technical details of the research project was held with Otis Wood, Bob Troxler and Larry Stuber of the Environmental Protection Division on August 27. Two items brought up at the meeting should be noted.

It was suggested that per cent of materials which are part of solid waste should be included in the table prepared in phase 1. This will be attempted to give a complete picture of the ways in which chemicals leave carpet mills.

Mr. Wood reported that the Southernal Regional Office of the Environmental Protection Agency plans a study of the Coosa River Basin during low flows in October. He requested a list of materials which should be considered when this study is conducted. We will attempt to prepare such a list and present it in the September monthly report.

References

1. Bowen, D. A., Textile World, 123, 63 (1974).

2. Multicoloration of Carpets by Continuous Procedures; Turner, Larson, Tokely; Dyes and Chemicals Bulletin (DuPont) 26: 77-91 Dec. 1970.

3. Multilevel Dyeing of Nylon Carpet Yarns; Bulletin C 19 (Allied Chemical) Jan. 1973.

4. Cadon Contract Carpets; Bulletin N11 (Monsanto).

5. Dyeing and Finishing Deep Dyeing Encron, Bulletin PSD2 (American Enka) Nov. 1970.

6. Piece Dyeing Carpets of DuPont BCF Nylon in Solid Shades; Bulletin N223 (DuPont) Jan. 1968.

7. Enka Nylon Carpet Yarns; Bulletin NECI (Enka) March 1970.

8. Carpet Technology; Bulletin N7 (Monsanto) Jan. 1965.

9. Dyeing Polyester Pile Carpets; Blackburn (I.C.I.) Textile Manufacturer 100; 33,34,37,39,41 (Feb. 1973).

10. Continuous Dyeing of Polyester Carpet; Forrester and Le Blanc (Tennessee Eastman) American Dyestuff Reporter 61: 29-32 (1972 June).

11. Review of Batch Dyeing of Polyester Carpet; Dyes and Chemicals Bulletin (DuPont) 28: 97-103 (July 1972).

12. Carpet Printing Technology; Sasseville (Ciba-Geigy) Canadian Textile Journal 89: 155-157 (April 1972).

13. Dye Variant Dacron and Acrilan Carpet Yarns for Winch Dyeing; Stewart (I.C.I.) International Dyer 147: 524-527 (May 1972).

TABLE 1

Fiber Usage in the Carpet Industry

Fiber	Volume 1973 (million pounds)	Volume 1978 (million pounds)	Dyeing Process			
			Yarn	Beck	Continuous	Print
Wool	50	50	X			
Cotton & Rayon	40	5	X	X		
Nylon	1,219	1,925	X	X	X	X
Acrylic/mod.	177	210	X			
Polyester	199	325	X	X	X	
Polypropylene	109	163	X			
TOTALS	1,794	2,678				

TABLE 2

Basic Chemicals in Dyeing

Dyes

Auxilaries

Carriers
Detergents
Retarders
Dispersing Agents
Thickeners
pH Control Additives
Antifoaming Agents
Chelating Agents
Fungicides
Softeners

Other

Lubricants
Antistatic Agents
Fire Retardants
Tints
Oligomer
Optical Brighteners
Fungicides

TABLE 3

Finishing Components

Latex

Rubber
Filler
Thickeners

Foam (Rubber, PVC, Urethane)

Rubber
Curing Agents
Blowing Agents
Thickeners
Filler
Plasticizers

TABLE 4

Dyes of Known Structure Commonly Used

For Nylon Carpet

Acid Dyes

Acid Yellow 17	Acid Blue 23
Acid Yellow 23	Acid Blue 25
Acid Yellow 25	Acid Blue 27
Acid Yellow 38	Acid Blue 40
Acid Orange 45	Acid Blue 45
Acid Red 37	Acid Blue 98
Acid Red 66	Acid Blue 80
Acid Red 80	Acid Blue 92
Acid Red 151	Acid Blue 113
Acid Violet 48	Acid Black 52

Mordant Dyes

Mordant Orange

Direct Dyes

Direct Yellow 44

Disperse Dyes

Disperse Yellow 3	Disperse Red 17
Disperse Orange 2	Disperse Blue 3
Disperse Red 1	Disperse Blue 7
Disperse Red 12	

TABLE 5

Dyes of Known Structure Commonly Used

For Acrylic Fiber

Basic Dyes

Basic Orange 21	Basic Blue 4
Basic Orange 22	Basic Blue 7
Basic Blue 3	Basic Green 4

TABLE 6

Dyes of Known Structure Commonly Used

For Polyester Fiber

Disperse Dyes

Disperse Orange 13

Disperse Red 11

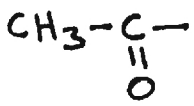
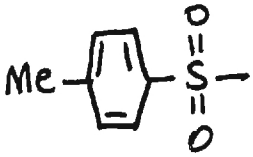
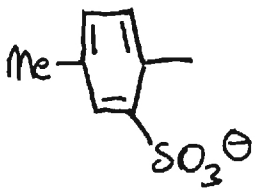
Basic Dyes

Basic Yellow 11

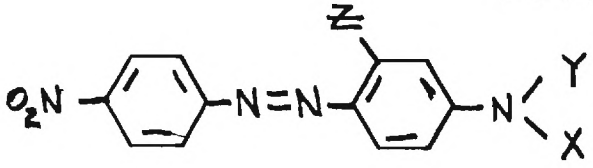
APPENDIX A

Chemical Abbreviations

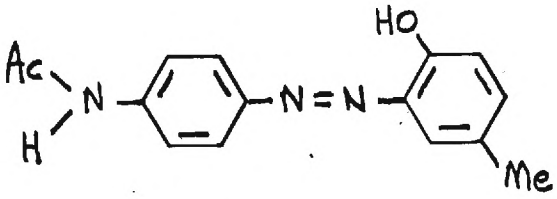
(often used with dyes)

Comman name	Chemical structure	Abbreviation
Acetyl		Ac–
Methyl	CH_3-	Me–
Ethyl	CH_3CH_2-	Et–
Phenyl		Ph–
Tosyl		Tos–
Ethylol	$HOCH_2CH_2-$	HOEt–
2-sulfo-4-methyl phenyl		SMP–

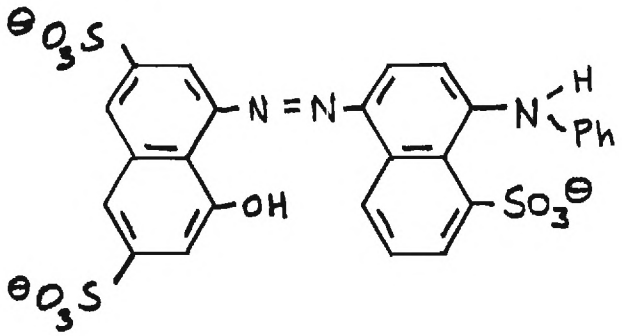
Comman Dyes



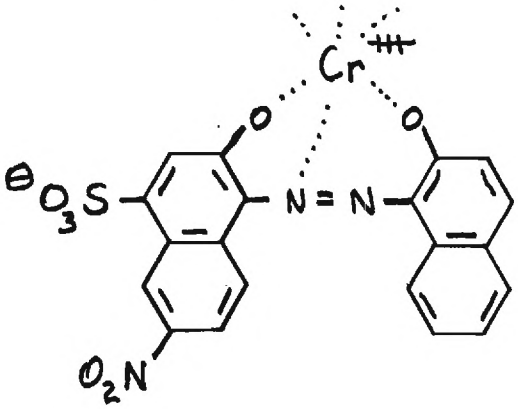
	X	Y	Z	Color Index
Disperse Orange 3	H	H	H	11005
Disperse Red 1	Et	EtOH	H	11110
Disperse Red 17	EtOH	EtOH	Me	11210



Disperse Yellow 3 — 11855



Acid Blue 92 (reddish) — 13390



Acid Black 52 — 15711

sold as a mixture of 2:1 and 1:1 complex usually 2 atoms chrome to 3 molecules dye

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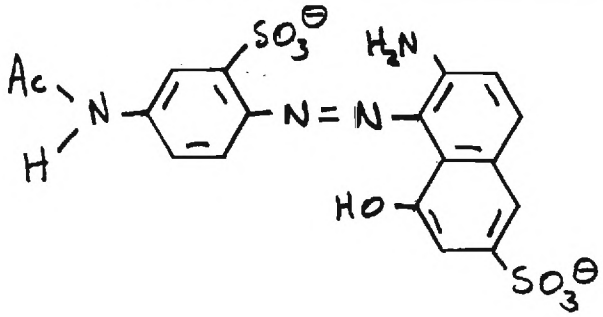
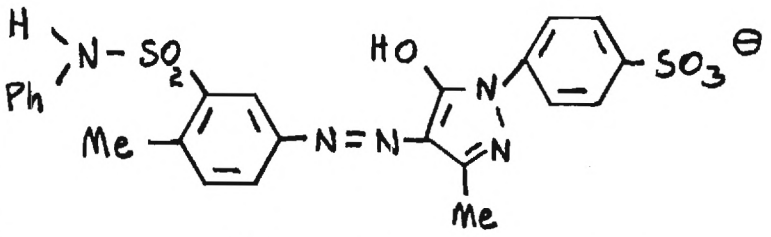
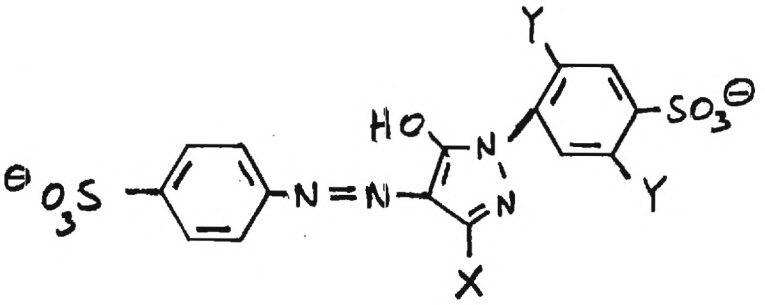


Acid Red 37 (bluish) — 17045

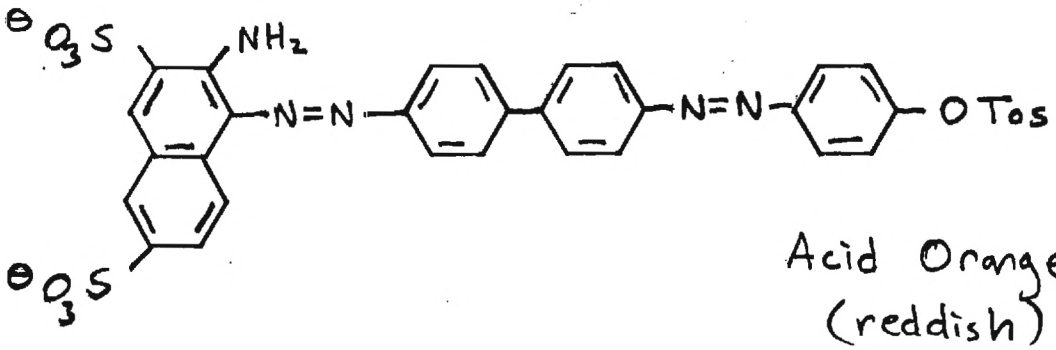


Acid Yellow 25 18835

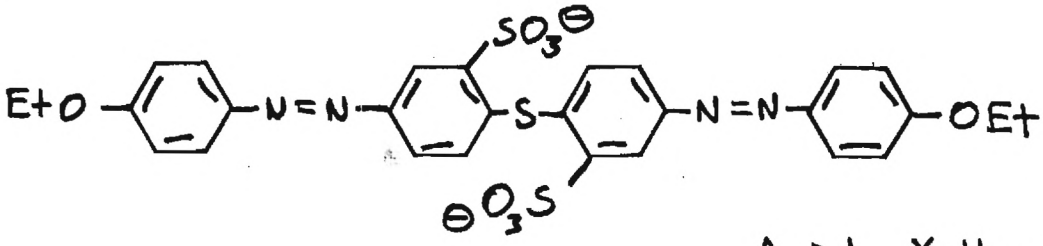


Acid Yellow 17 18965
(bright yellow)
X = Me Y = Cl

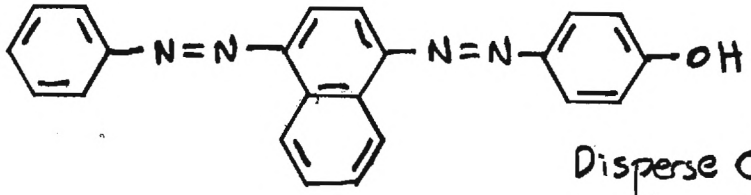
Acid Yellow 23 19140
X = $COO^{\ominus}$ Y = H



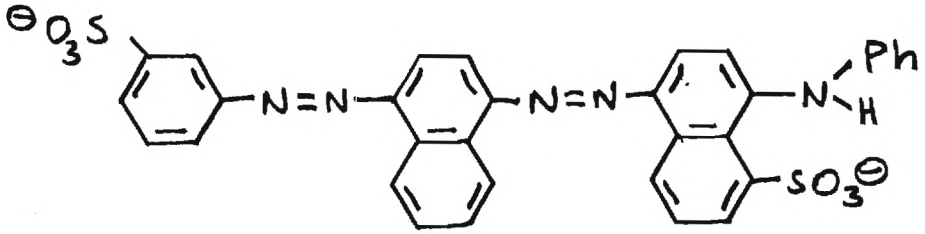
Acid Orange 45 22195
(reddish)



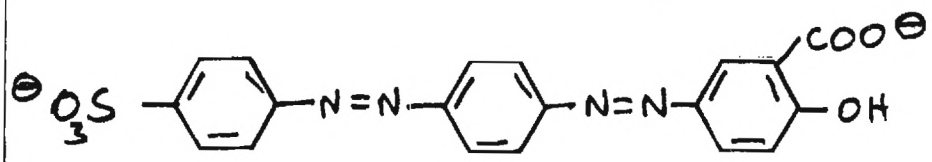
Acid Yellow 38 25135



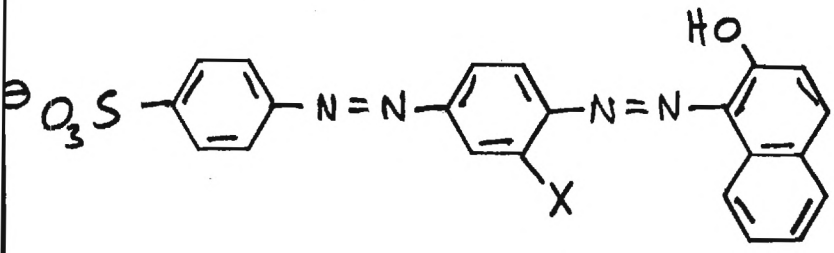
Disperse Orange 13 26080
(yellowish)



Acid Blue 113, 26360
(Reddish navy)

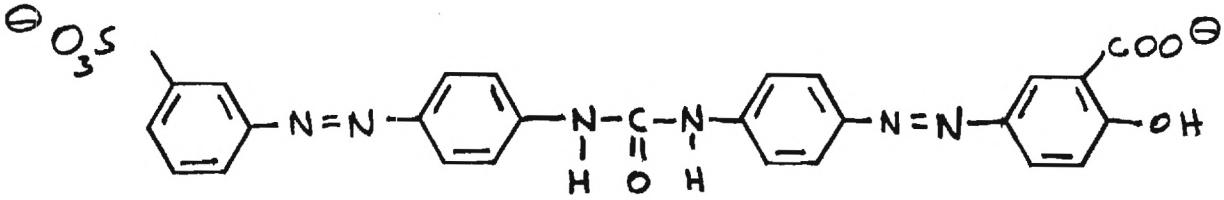


Mordant Orange 6
(Pull reddish) 26520

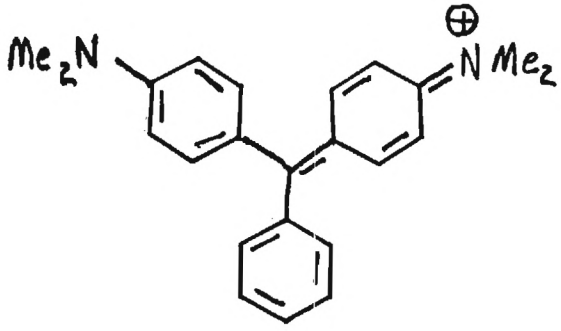


Acid Red 151 26900
X = H

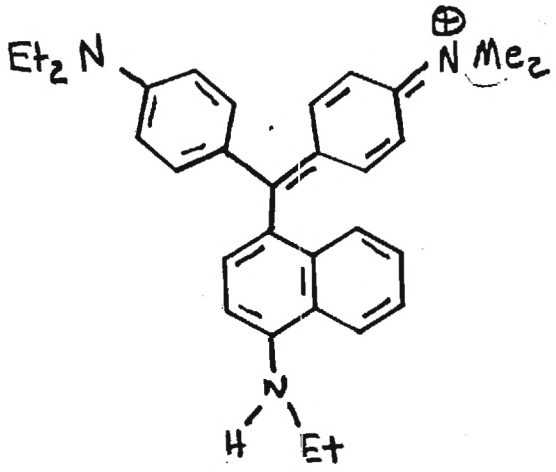
Acid Red 66 26905
(yellowish)
X = $SO_3^{\ominus}$



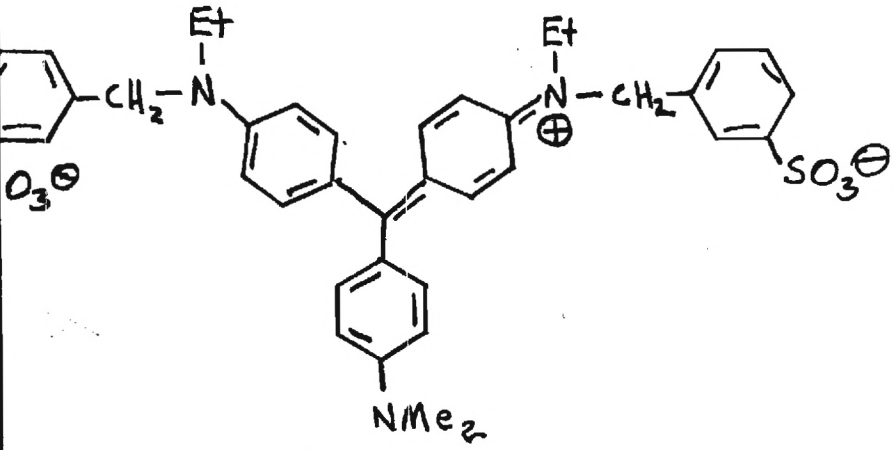
Direct Yellow 44 29000
(Bright yellow)



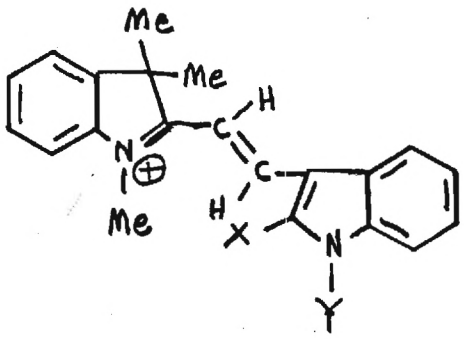
Basic Green 4 42000
(Bright bluish)



Basic Blue 7 42595
(Bright reddish)

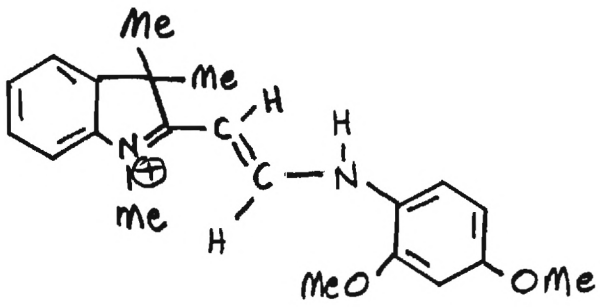


Acid Violet 49 42640
(Bright bluish)

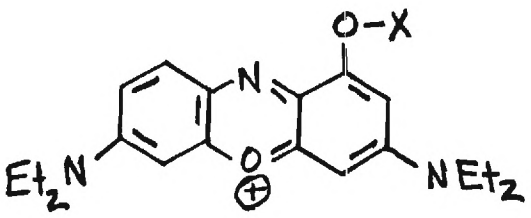


Basic Orange 21 48035
(Bright yellowish)
Y = H X = Me

Basic Orange 22 48040
(Bright orange)
Y = Me X = Ph

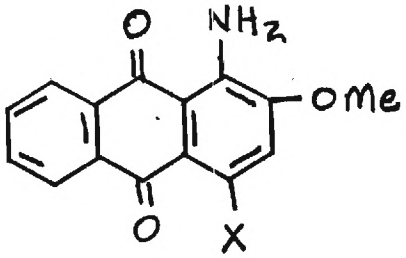


Basic Yellow 11 48055
(Bright yellow)



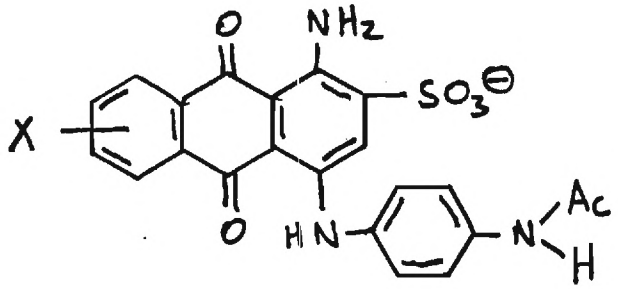
Basic Blue 4 51004
(Bright Greenish) X = Me

Basic Blue 3 51005
(Bright Greenish) X = Et



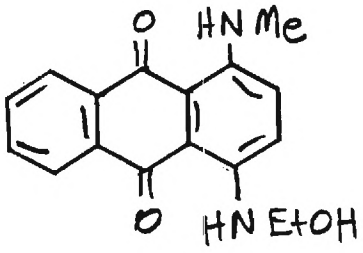
Disperse Red 4 60755
(Bright pink) X = OH

Disperse Red 11 62015
(Bright bluish pink) X = NH2

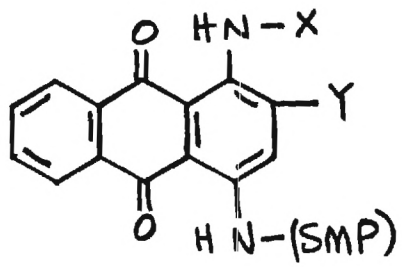


Acid Blue 23 61125
(Greenish) X = H

Acid Blue 40 62125
(Greenish) X = $SO_3^{\ominus}$

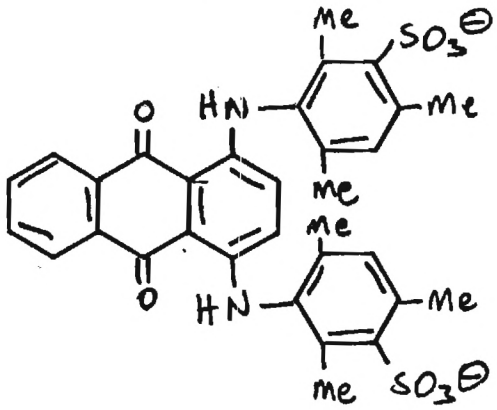


Disperse Blue 3 61505
(Bright blue)

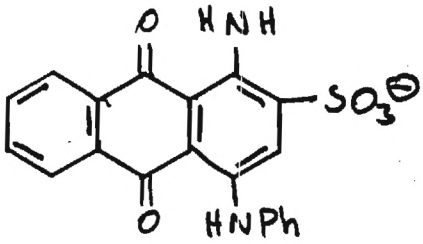


Acid Blue 27 61530
(Greenish) X= Me Y=H

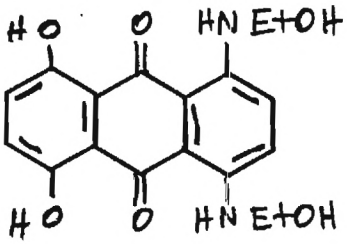
Acid Blue 78 62105
X= H Y=Br



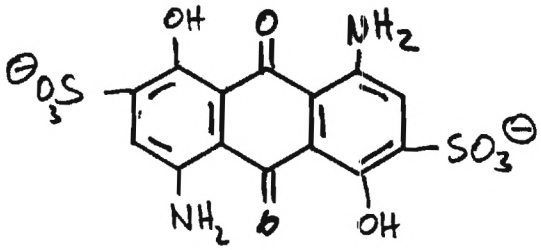
Acid Blue 80 61585



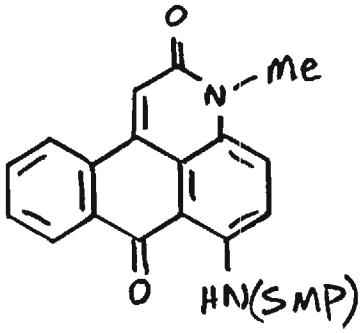
Acid Blue 25 62055



Disperse Blue 7 62500
(Bright Greenish)



Acid Blue 45 63010



Acid Red 80
(Bright Bluish)

68215

File: E-27-626

Monthly Progress Report Number 2

(Sept. 15 - Oct. 15, 1974)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division

Department of Natural Resources

State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher

School of Textile Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward further quantification of the quantities of dyes used in carpet processing and discharged in spent dye baths. Initial work has also begun on dyeing auxiliaries and other chemical species used in carpet processing. An initial list of chemicals used in large volume in beck dyeing of carpet has been compiled to assist in the current stream survey being conducted jointly by the Environmental Protection Agency Athens Laboratory and the Georgia Department of Natural Resources.

II. Typical Dye Bath Composition in Beck Dyeing

As indicated in Table 1, Nylon, Acrylic, Polyester, and Polypropylene fiber account for the bulk of the carpet produced in the United States. Essentially all acrylic and polypropylene fiber is either producer colored or is dyed by yarn manufacturers. Beck dyeing therefore is limited almost exclusively to polyester and nylon carpets. Polyester is dyed only with disperse dyes and nylon can be dyed by either acid or disperse classes of dyes. The chemical composition of the dye baths for polyester dyed with disperse dye is shown in Table 2, for nylon dyed with disperse dyes in Table 3, and nylon dyed with acid dyes in Table 4. Typical types of chemical materials used for the various functions indicated in Tables 2, 3 and 4 are shown in Table 5.

An attempt has been made to get a first estimate of the quantities of chemical auxiliaries used in beck dyeing of carpet. These estimates are shown in Table 6. Also included in Table 6 is an estimate of the quantities

of these materials discharged annually in spent dye baths and rinse water. These estimates are based on fiber consumption as reported for 1973. These figures may be modified somewhat when printing and continuous dyeing are considered, however, preliminary information suggests that essentially the same types and quantities of these materials are used in continuous dyeing and printing. Some materials (particularly thickneners)are used in addition to the materials shown in Table 5 in the continous processes.

III. Quantities of Dyes Discharged

An attempt has also been made this month to get an estimate of the types and quantities of dyes discharged by the carpet industry. The results are shown in Table 6. The dyes shown in Table 6 are referred to in the industry as "workhorse dyes".

The estimates in Table 7 were obtained by examining dye formulations recommended by fiber and chemical suppliers production records of carpet manufacturing companies, and production data for the dye manufacturing industry. Although the quantity of dyestuff used in the bath varies extensively from color to color, an average quantity of 1.3% based on face yarn weight is a good estimate of the total quantity consumed.

The dye quantities used in processing polyester fiber (by beck dyeing) in Table 6 are believed to be very good estimates. They were obtained by comparison of recommended dye lists from the three leading polyester carpet fiber producing firms, several dyestuff manufacturers, and the leading chemical auxiliaries manufacturer. The list was further checked by comparison of actual production records on dyeing of over 11 million

pounds of polyester fiber (approximately 6% of the total production in 1973). Quantities of each dye used in the processing of the 11 million pounds of polyester was multiplied by 17 to obtain the consumption data shown in Table 6. The activity and quantity remaining in the dyebath after the dye cycle are estimates based on industry experience.

Data on dyes used to color nylon carpet is on a less firm basis. Production data on only 7 million pounds (less than 1% of the total production) was available for these estimates so a number of assumptions were necessary in the computation of consumption figures. These figures will be revised as more data become available.

It should be noted that only 12 dyes account for over 80% of the dyestuff used in beck dyeing of carpet. The agreement of data from many sources suggest that these 12 dyes are truly "workhorses" and do account for the bulk of carpet beck dyeing.

Future Work

During the coming month major effort will be directed toward assessing the dyes and chemical auxiliaries used in continous processing of carpet, including printing.

TABLE 1

Fiber Usage in the Carpet Industry

Fiber	Volume 1973* (million pounds)	Volume 1978 (million pounds)	Dyeing Process			
			Yarn	Beck	Continous	Print
Wool	40	50	X			
Cotton & Rayon	67	5	X	X		
Nylon	1,000	1,925	X	X	X	X
Acrylic/mod.	141	210	X			
Polyester	186	325	X	X	X	
Polypropylene	82	163	X			
Other	4	-				
TOTALS	1,520	2,678				

Actual consumption in 1973 as indicated by the

*Carpet and Rug Institute Annual Report. Data in the first project report was projected from 1972 figures.

TABLE 2

BECK COMPOSITION FOR DYEING

POLYESTER CARPET

Chemical	% Based on Face Yarn Weight
Dye	1.3
Chelating Agent	0.5
Dispersing Agent	1.0
Wetting Agent	0.5
pH Control Agent	2.0
Carrier	7.0

TABLE 3

BECK COMPOSITION FOR DYEING

NYLON CARPET WITH DISPERSE DYES

Chemical	% Based on Face Yarn Weight
Dye	1.3
Chelating Agent	0.5
Dispersing Agent	1.0
Wetting Agent	0.5
pH Control Agents	2.0

TABLE 4

BECK COMPOSITION FOR DYEING

NYLON WITH ACID DYES

Chemical	% Based on Face Yarn Weight
Dye	1.3
Chelating Agent	0.5
Dispersing Agent	1.0
Wetting Agent	0.5
pH Control Agents	2.0

TABLE 5

Chemical	Use	Consumed in 1973 (1000 pounds)	Acitvity Wt. Active Ingr. / Wt. Comm. Prod.	Unexhausted Wt. in Bath, End / Wt. in Bath, start	Discharge in 1973 (1000 pounds)
Ethoxylated primary and secondary alcohols typically C- 6 to 12 with 6 to 12 moles ethyleneoxide	leveling agent wetting agent scouring agent for oily soil	4,150	1.0 plus 15% of all Biphenyl	1.0	4,150
Aryl sulfonates (usually sodium salts) typically Dodecylbenzene sulfonate Naphthalene sulfonate Diphenyloxide disulfonate	leveling agent, acid dyes wetting agent dispersing agent, disperse dyes retarder, acid dyes scouring agent for particulate soil	2,900	1.0	0.8	1,850
Acetic acid	pH control (3.5 attainable) continuous dyeing and printing nylon stock and yarn dyeing nylon and acrylic beck dyeing polyester stripping	1,350	1.0	0.8	1,080
MSP	pH control (4.8 attainable) beck dyeing	1,050	1.0	1.0	1,050

Chemical	Use	Consumption	Activity	Unexhausted	Discharge
Lignin sulfonate (sodium and calcium salt) a complex mixture of sulfonates of coniferyl alcohol based oligomers (source disperse dyes)	Dispersing agent, disperse dyes	1,150	15% of all disperse dyes	1.0	1,150
Nylon oligomer poly (hexamethylene-adipamide) of molecular weight 400 to 2000 (source fiber extractives)	Fiber extractive	1,000	1% of all nylon fiber	1.0	1,000
Ethoxylated phenols Nonyl and octyl phenol with 6 to 12 moles ethyleneoxide terminating in a $-CH_2CH_2OH$ group	Leveling agent, disperse dyes scouring agent for oily soil	830	1.0	1.0	830
Ethoxylated phenols - sulfated (usually ammonia salt) Ethoxylated phenols terminating in a $-CH_2CH_2OSO_3NH_4$ group	Foaming agent wetting agent	800	1.0	1.0	800
TSP Trisodium phosphate	pH control (10.5 attainable) beck dyeing nylon	710	1.0	1.0	710
Sodium Chloride	exhaustion aid for backing colors and acid dyes	690	1.0	1.0	690

Chemical	Use	Consumption	Activity	Unexhausted	Discharge
Biphenyl typical diluents are emulsifier ethoxylated alcohols, and fatty acid	carrier(plasticizer) for polyester	12,850	0.8	0.01	102
Alcohol sulfates and phosphates typically C-8 to 10 linear and branched primary alchohols	wetting agent leveling agent, acid dyes	400	0.8	0.8	256
Sulfated Oils typically sulfated Ricinoleic acid tri-glyceride	wetting agent leveling agent, acid dyes	400	0.8	0.8	256
Fatty acid ethanolamines typically the 1 to 1 adduct of lauric acid and diethanolamine	Emulsifying agent for oils and make up agent for carriers and lubricants	642	5% of all Biphenyl	0.8	514
Alkyl quarternary salts (usually the chlorine salt) typically C-12 to 16 fattyamine - with three methyl to ethly functions (source antistatic finish on fiber)	Antistatic finish	500	1/2 of all fiber	0.8	400

Chemical	Use	Consumption	Activity	Unexhausted	Discharge
EDTA Ethylene Diamine Tetraacetic Acid	sequestering agent for non ferrous ions	400	0.04	1.0	160
Ethoxylated alkylamines typically C-16 to 18 fatty acid/ethylenediamine or propylenediamine adduct which is ethoxylated 1 to 4 moles	softeners lubricant	1180	1.0	0.1	118
Antifoams at this time there is a change from silicone oil to minearl oil and linear alchohol antifoams due to changes in flammability requirements. Their consumption will be covered in a later report	antifoam	1500	-	-	-

TABLE 6

CONSUMPTION AND DISCHARGE OF "WORKHORSE" DYES

DYE	USE	Consumed in 1973 (1000 pounds)	Activity Wt. Active Ingr. / Wt. Comm. Prod.	Unexhausted Wt. in Bath, End / Wt. in Bath, start	Discharge in 1973 (1000 pounds)
Disperse Yellow 3	Nylon	2704	0.85	.05	115
Disperse Red 55	Nylon	1058	0.85	.10	90
Disperse Yellow 23	Polyester	716	0.85	.05	30
Disperse Yellow 54	Polyester	677	0.85	.05	29
Disperse Blue 7	Nylon	571	0.85	.20	97
Disperse Red 60	Polyester	402	0.85	.10	34
Disperse Blue 120	Polyester	361	0.85	.20	61
Acid Yellow 19	Nylon	243	0.85	.02	4
Disperse Orange 59	Polyester	238	0.85	.05	10
Disperse Blue 3	Nylon	191	0.85	.20	32
Disperse Yellow 42	Polyester	172	0.85	.05	7
Acid Red 151	Nylon	167	0.85	.02	3
Acid Red 167	Nylon	162	0.85	.02	3
Disperse Red GN	Polyester	115	0.85	.10	10
Acid Blue 40	Nylon	109	0.85	.02	2
Disperse Red 1	Polyester	105	0.85	.10	9
Acid Yellow 38	Nylon	98	0.85	.12	2
Disperse Blue CRS	Polyester	90	0.85	.20	15
Acid Red 57	Nylon	76	0.85	.02	1
Disperse Blue 56	Polyester	71	0.85	.20	12
Basic Yellow R2	Nylon	62	0.85	.02	1
Disperse Yellow 87	Polyester	44	0.85	.05	2
Disperse Red 65	Polyester	36	0.85	.10	3
Disperse Blue 118	Polyester	30	0.85	.20	5
Disperse Blue 60	Polyester	29	0.85	.20	5
Disperse Red 86	Polyester	13	0.85	.10	1

E-27-626

Monthly Progress Report Number 3

(Oct. 15 - Nov. 15, 1974)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division

Department of Natural Resources

State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher

School of Textile Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward assembling data on printing and continuous dyeing of carpets. These methods of carpet coloration are relatively new technologies and are expected to be used for even larger volumes of carpet production in the future than they are at the present time.

The technology for coloring nylon carpets by printing and continuous processing is reasonably well developed. Techniques for printing and continuous dyeing of polyester carpets are in an early stage of development. One or two companies are reported to be processing polyester carpets by these procedures but industry sources indicate that the volume is very small. Larger volumes of polyester carpet will probably be colored by these techniques in the future as the technology develops.

The more popular continuous dyeing and printing processes employed by the U.S. carpet industry are described below. Quantities of chemicals used and typical chemical species employed in these processes are also given.

II. Carpet Printing

Two major types of printing machines are employed in carpet printing. One type uses either flat bed or rotary screen with dye being applied to the carpet by squeezing a thickened dye mixture through holes in a patterned screen. The second type of process

uses a roller type application which applies dye from a raised sponge covered patterned roll. Screen printing is used for by far the largest volume of carpet printing in the U.S. The Zimmer Printing Machine is most frequently used with 23 flat bed and 6 rotary screen units either installed or on order by U.S. carpet companies. The Stalwart Printer (a roller sponge type) accounts for the bulk of the remainder of the printed carpet with 6 machines currently in operation.

A. Screen Printing

In screen printing the dye is applied to the carpet in the form of a thick paste. The printed carpet then passes to a steamer where the carpet is heated to the dyeing temperature and the dyestuff transfers from the paste to the fiber and diffuses into the fiber. The final step is an afterscour and rinse to remove residual dyestuff followed by drying.

A typical print paste composition for screen printing is shown in Table 1. The gums used in print paste are usually of natural origin such as modified locust bean, or guar gum. Chemically the products used are hydroxyethyl and carboxymethyl ethers of galactomannan polysaccharides. Preservatives used are generally chlorinated phenols or chlorinated phenol derivatives. The dyeing assistants employed will depend on the specific carpet being printed but will generally be anionic or nonionic surfactant. Small quantities of other chemicals are used in "dispersion" of the dyestuff prior to their addition to the print paste. Diethylene glycol, Kromfax (thiodiethylene glycol),

Table 1

Screen Printing Print Paste

Gum	1.0%*
Preservative	0.4%
Dyeing Assistant	1.0%
Benzyl Alcohol	2.0%
Formic Acid (87%)	1.0%
Dyes	1.0%

Pick-up 200% Based on Face Yarn Weight

and small quantities of wetting agents are commonly used.

Dyes used in printing are primarily in the acid class. Many of the dyes are similar to those used in beck dyeing (Acid Blue 40, Acid Blue 25, etc.) Some, however, are not used extensively for beck dyeing and will require further investigation.

Table 2

Stalwart Printing Print Paste

Gum	0.4%
Preservative	0.3%
Dyeing Assistant	1.0%
Acetic Acid (56%)	1.0%
Dyes	1.0%

Pick-up 200% Based on Face Yarn Weight

* Concentrations for all tables in this report are % on-weight of solution.

B. Stalwart Printing

Print paste used in Stalwart Printing has the composition shown in Table 2. Materials that are used are very similar to those employed in screen printing. Somewhat smaller quantities are required for Stalwart printing.

C. Quantities of Chemicals used in Printing

A survey of industry sources suggests that 5-10% of nylon carpet is now printed. Since only nylon is printed, approximately 50,000,000 pounds of carpet yarn are printed. Based on this volume the estimated chemical use is shown below:

Gum	1,000,000 - 2,000,000 pounds
Perservatives	400,000 - 800,000 pounds
Dyeing Assistants	1,000,000 - 2,000,000 pounds
Benzyl alcohol	2,000,000 - 4,000,000 pounds
Formic acid	1,000,000 - 2,000,000 pounds
Dyes	1,000,000 - 2,000,000 pounds

III. Continuous Processing of Carpets

The Kuster continuous dyeing range has captured almost the entire market for continuous dyeing of carpet. Approximately 23 Kuster units were either ordered or installed in the U.S. last year. At 70% efficiency these units could process approximately 200,000,000 square yards of carpet. An estimated 900,000,000 square yards of carpet were produced in 1973 so that approximately 25% of all carpet produced could be dyed on continuous units.

Nylon carpet is the major type dyed on continuous units. Two carpet manufacturers are reported to be dyeing polyester carpet on Kuster units but the volume being dyed continusly is probably small.

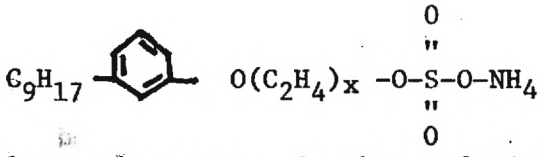
An important modification to the Kuster continuous units is a device which permits dropping dye in irregular patterns on the carpet. This is commonly referred to as TAK dyeing. Approximately 16 of the Kuster continuous ranges in the U.S. are equipped with TAK dyeing units.

A. Kuster Dyeing

Continuous dyeing on the Kuster unit requires three wet processing steps - prewetting, dye application, and afterscouring. Compositions of these baths are shown in Table 3. Typical prewetting bath additives are sodium dioctyl sulphosuccinate

$$C_8H_{17}\text{-}COO\text{-}CH_2\text{-}CHSO_3Na\text{-}COO\text{-}C_8H_{17}$$

and low mole ethylene oxide adduct phenols or alcohols. Foaming agents are generally mixtures of anionic and nonionic surfactants in many cases identical to the compounds used in the prewetting steps. The ammonium salt of sulphated nonionic detergents are also used



Modified locust bean gum is the predominant product used as a thickener in Kuster dyeing. A nonionic detergent is used in the afterscour.

Acid and direct dyes are used most exclusively in Kuster dyeing of nylon. A typical list of common dyes is shown in Table 4. In some tone-on-tone dyeings, cationic dyeable nylon is used and the dyes at the bottom of Table 4 may be employed.

The volume of carpet being processed on continuous Kuster units appears to be highly variable. It is estimated at the present time that 40% of all carpet processed is being dyed continuously. This percentage will drop with an increase in carpet production. In periods of low production, carpet dyeing shifts from beck to continuous processing. The major difference this will produce is in quantities of gums and perservatives being used and a somewhat different mixture of dyes. A better estimate of the quantities of carpet being processed on Kuster units will be attempted in the next few months.

TABLE 3

Chemical Usage in Kuster Dyeing

Prewet Bath	
Wetting agent	.3%
Pick-up	100%
Dye Pad	
Foaming Agent	.3 %
Thickener	.25 %
Preservative	.2 %
Monosodium Phosphate	.2 %
Acid Dyes	.3 %
Pick-up	300-400%
After Scour	
Nonionic Detergents	.2%

TABLE 5

TYPICAL TAK DYEING FORUMULATION

Thickener	.5-1.5%
Wetting Agent - Foaming Agent	.0-.5%
Formic Acid (87%)	.5-1%
Dyes	.2-.3%

Table 4

Dyes Used in Kuster Dyeing

Acid Yellow 174	Acid Red 337	Acid Blue 40
Acid Yellow 175	Acid Red 266	Acid Blue 25
Acid Yellow 159	Acid Red 151	Acid Blue 145
Direct Yellow 44	Direct Red 37	Acid Blue 122
Direct Yellow 12	Direct Red 39	
Acid Orange 132	Direct Red 1	
Acid Orange 128	Acid Red 37	
Direct Orange 59	Acid Red 73	
Acid Yellow 17		
Acid Yellow 38		
Basic Yellow 11	Basic Red 17	Basic Blue 21
Basic Yellow 31	Basic Red 47	Basic Blue 22
Basic Yellow 15		
Basic Orange 25		

B. TAK Dyeing

A typical TAK dyeing formulation is shown in Table 5. The materials used in TAK dyeing are very similar to those employed in Kuster dyeing volume processed TAK dyeing will also require further quantification.

IV. Future Work

Visits are planned to 3 other carpet manufacturers to conclude the first phase of the research project.

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E-27-626

Monthly Progress Report Number 4
(Nov. 15, 1974 - Dec. 15, 1974)

Identification & Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

In previous monthly reports the dyes and auxiliary chemicals used in beck dyeing, continuous dyeing, and printing of carpets have been discussed. Two other major areas of chemical usage which are potential sources of pollution are the latex materials used in carpet backing and the chemicals present in carpet yarns as supplied by the fiber manufacturers and which may be extracted in the dye bath. Latex composition and usage will be discussed this month and data on chemicals present in carpet yarn will be given in the January report.

II. Latices used by the carpet industry

A. Use of Latices

Latex is used on tufted carpets to prevent detufting from the primary backing and to make carpet heavier, stiffer, and more dimensionally stable. Woven carpets (which accounts for only 3% of production) require only the latter function since the former function is accomplished in the weaving. The latex may be foamed to provide an underlay or used as a precoat adhesive to adhere a separate foam or a secondary backing fabric. Lamination of secondary backing shown in figure 1, is the most common construction as indicated by the data of table 1.

Figure 1 Tufted carpet construction

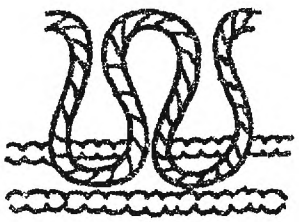


Table 1 Estimated Latex consumption in 1973

Use	pounds of latex formulation (x 10^6)
Secondary lamination	850
Precoat adhesive	80
Foam underlay	140
Primary binder only	90

As indicated below, the chemical structure of the latex employed is dependent on the use to which the carpet is to be put; whereas it is primarily the chemicals added to the latex formulation which determines whether it is used for laminating, precoating, foaming or primary binding.

B. Chemical Structure of Latices

The chemical nature of latices used on carpet is indicated in table 2. The carboxylated styrene - butadienes (or CSB's) account for 80% of all consumption. The CSB's are sold as water emulsions at about 50% solids with 1% emulsifier and 1% antioxidant present. The copolymer is 50 $\pm$ 10% styrene with 2% carboxy containing monomer, typically acrylic acid.

The latices other than CSB's are used for special applications. Polyethylenes for example are applied by hot melt and provide a product which can be molded to fit the contours of an auto interior. Polystyrene - butadienes are often used as primary binders to produce a non-slip backing for area rugs. Formulations for non-slip backings are similar to lamination formulations but with filler omitted. Polyvinyl chloride and polyvinyl acetate-enthylene use will increase due to their inherently better flamability characteristics than the CBS's.

Table 2 Latex structure

Chemical structure (see appendix)	Principle Use
Polycarboxylated - Styrene - Butadine	Indoor carpet
Polystyrene - Butadine	Area rugs
Polyethylene	Automotive carpet
Polyvinyl acetate - Ethylene	Institutional carpet
Polyvinyl chloride	Outdoor carpet
Polyisoprene (natural rubber)	Blended with other latices

C. Latex Formulations

Table 3 lists typical formulations. The amount of mechanically foamed latex used has fluctuated as ecconomics and consumer acceptance of non-fibrous underlay changed. The range of this fluctuation has been between 20 to 50% foamed underlay.

Table 3 Latex Formulation

Agent	Laminating	Foaming
Latex	25%	46%
Buffer	.2%	.2%
Thickener	.3%	
Filler	75.5%	45.8%
Foaming agent		2%
Gelling agent		3%
Vulcanization agents		3%

Typically latices for foaming are mixtures of about 70% CSB 30% polyisoprene, where as 100% CSB is often used for laminating. Buffers are typically tetra sodium pyrophospate or trisodium phosphate. Common thickeners are acrylic acid copolymers and carboxymethylated cellulose. Fillers are aluminum silicate based clays and ores, calcium carbonate, and more recently alumina trihydrate which reduces flamability. Typically sodium oleate is the foaming agent. The principle vulcanization agent is the accelerator which may be an inorganic such as zinc

oxide or organic such as 2-mercaptobenzothiazole.

A mixture of ammonium acetate and zinc ammine when heated releases the zinc to form divalent branch salts with the latex which gels the foam. The current trend is to replace the ionic gel agents in these foam formulations with covalent gel systems. This can be done, but more slowly, by formation of covalent branches with monomers such as melamine. The advantage of these newer covalent "no gel" formulations is that they are more stable in holding tanks. This means that the amount of prematurely gelled formulations which must be disposed of should decrease as the trend is toward increased use of the "no gel" formulation method.

III. Polution Loads from Latices

Latex chemicals find their way into the environment through spills, land fill leach out, and partial formulations which are found to be defective. This makes it difficult to estimate the quantity of these chemicals which might be found in the water environment. The quantities of the significant chemicals used in latex formulation are summarized in Table 4.

Table 4 Estimated Consumption for 1973 of Latex Chemicals which Might be Significant Pollutants

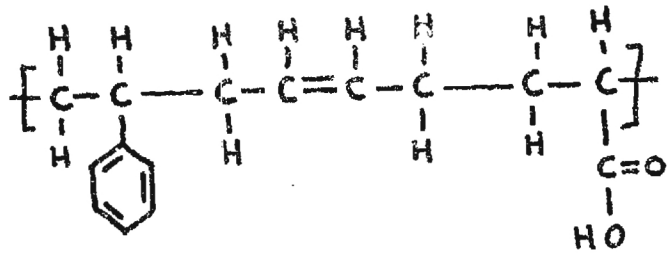
Chemical	Pounds x 10^6
Filler	470
CSB	220
Polystyrene - Butadine	50
Polyisoprene	10
Gel agents	20
Accelerators	20

IV. Future Work

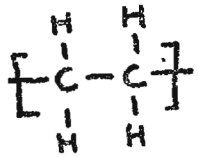
Extensive processing data from a large carpet manufacturer (annual consumption of face yarn-12 million pounds) has been obtained and is being analyzed. Results will be reported next month. Competion of the first phase of the project is planned for Mid-February.

Appendix

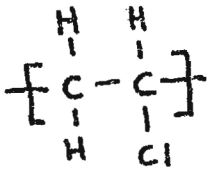
Chart of Structures



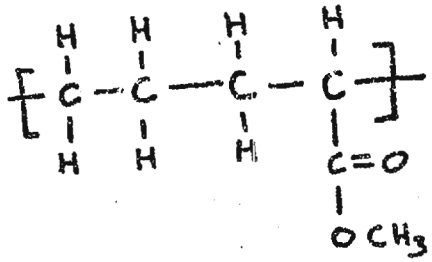
CSB



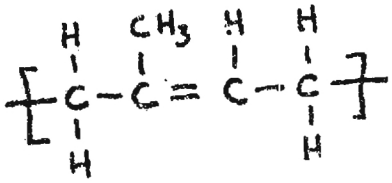
Polyethylene



Polyvinylchloride



Polyacetate - ethylene



Polyisoprene

E-27-626

Monthly Progress Report Number 5
(Dec. 15, 1975 - Jan. 15, 1975)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

In previous monthly reports the various steps in carpet processing have been discussed and the types and quantities of various chemical species used have been listed. Efforts are now being directed toward completing the first phase of the project and initial experiments on Phase II, development of analytical techniques for stream analyses, are underway.

II. Status of Phase I

At the present time data on processing of over 11 million pounds of nylon and 15 million pounds of polyester carpet have been collected. Data include the various types of yarns processed and the quantities of the various chemcials used in dyeing and finishing. All data are from the period January 1, 1974, through September 30, 1974. In this period the carpet industry was operating at a reasonably conventional level so that data should reflect normal operating conditions. On an annual basis the data represent approximately 11% of the polyester carpet and approximately 2% of the nylon carpet produced during this period.

The data base for polyester carpet would appear to be more than adequate for the projections planned in this study. Data from one or two other principally nylon carpet producers are being sought to increase the representation of this important fiber in the data base.

In addition to data from carpet manufacturers, a leading producer of textile chemicals has agreed to supply a list of all chemicals sold during this period in the Dalton, Georgia area. This list should be available within the next month and will be valuable in determining actual chemical species present in formulations used in carpet processing.

During this month a visit was made to the Carpet and Rug Institute in Dalton and to RBI, Inc., a leading consulting firm in the carpet industry. These sources provided some information on the directions projected for carpet processing over the next five years.

An important type of data not readily available from carpet manufacturers is the efficiency in usage of processing chemicals (the partition of dyes and other chemicals between the dye bath and carpet). This partition will greatly influence the quantities of materials being sent to waste treatment facilities. Experiments have been started to collect this data for the more important dyes and anxiliary chemicals. Experiments have also been initiated to determine the identity and quantities of dispersing agents in formulation of the more important dyes.

The assembly and analysis of the remaining data should be completed by April 1 and a report on Phase I is planned for early April.

II. Status of Phase II

Based on tentative lists of the important dyes and processing chemicals, initial work is underway to develop analytical procedures for these materials. Absorption and fluorescence spectra of a number of dyes and carriers have been obtained and limits of detectability are being established. Gas chromatography and thin layer chromatography experiments will be initiated soon.

III. Personnel

Conduct of the experimental phase of the project has required the assistance of additional laboratory personnel. Two graduate students are now assigned to the project. These students are supported by Institute funds

and are not charged to the project budget. In addition, the services of a well trained chemist familiar with the carpet industry have been obtained and he is working half-time on this project.

E-27-626

Monthly Progress Report Number 6
(Jan. 15, 1975 - Feb. 15, 1975)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward completion of Phase I of the project and development of the necessary sampling and laboratory techniques for analyses of streams for carpet processing effluents.

II. Status of Phase I

Data on the processing of an additional 4.7 million pounds of nylon and 0.6 million pounds of polyester carpet have been obtained. This brings the total data base to approximately 16 million pounds each of both polyester and nylon carpet. Data on production of more nylon carpet is currently being sought.

Initial data on purity (% dye in the commercial sample) and per cent exhaustion (dye removed from the bath by the carpet in a typical dyeing) of several of the important dyes used in carpet processing have been obtained. These data are given in Table 1. The exhaustion data were obtained by carrying out test dyeing of nylon carpet under conditions currently used in the carpet industry. The results suggest that approximately 98% of the dye is removed by nylon carpet. These values are somewhat larger than had been anticipated. Similar data will be obtained for polyester carpet dyeings and for several additional dyes.

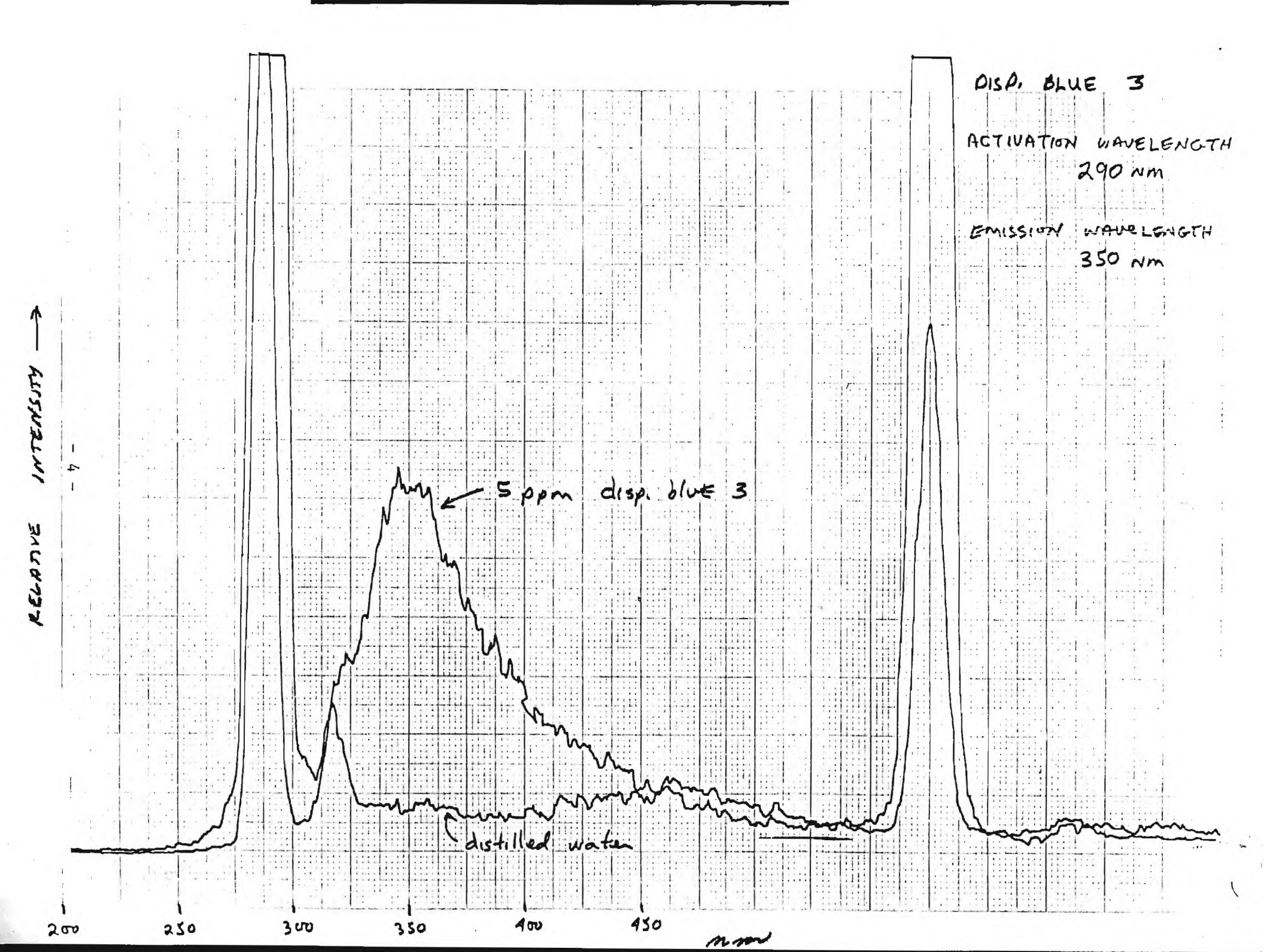
III. Status of Phase II

Fluorescence spectra of a number of dyes used in large volume for carpet processing have been obtained on the Aminco-Bowman Fluorescence Spectrophotometer. A typical spectrum is shown in Figure 1 for Disperse Blue 3 at 5 ppm

TABLE 1

Purity and Exhaustion Data For Selected Disperse Dyes

Dye	Exhaustion on Nylon (%)	Purity (%)
Blue 3	98	-
Blue 7	98	70
Red 1	98	91
Red 17	98	77
Yellow 3	98	-


DISP. BLUE 3
ACTIVATION WAVELENGTH
290 nm
EMISSION WAVELENGTH
350 nm
5 ppm disp. blue 3
distilled water
RELATIVE INTENSITY
200
250
300
350
400
450
nm

in water. The background spectrum for distilled water is also shown. The excitation peak occurs at 290 with emission at 350 nm. The peak at approximated 575 is due to second-order scatter of the exciting light. Very similar spectra were obtained for most of the disperse dyes investigated. These results are shown in Table 2. The similarity in the excitation and emission spectra of these disperse dyes despite rather wide differences in chemical structure suggested that the fluorescence was not orginating from the dyes themselves.

This hypothesis was tested by separation of the dyes into components by thin-layer chromatography. Dye solutions were spotted on silica gel plates and developed with an ether/cyclohexane/ethanol, 52/34/14, solvent mixture. The dyes readily migrated in the solvent mixture but the dispersing agent did not move. The spots were removed from the plates and the dyes extracted into chloroform and the dispersing agents extracted into water. Fluorescence spectra of the extracts confirmed that the observed spectra originate in the dispersing agent component. The spectra for pure Disperse Yellow 54 and its dispersing agent are shown in Figure 2.

A fluorescence emission near 360 nm has been previously reported (W. Tincher, "Effect of Polyester Fiber Processing Effluents on Water Quality" Final Report ERC-1673, Georgia Institute of Technology, November 1973) but unidentified in streams carrying waste from carpet processing plants. The present work strongly suggests that this peak is due to dispersing agents from disperse dyes used in the carpet industry.

TABLE 2

Fluorescence Spectral Data for 9 Disperse Dyes

Dye	Chemical Type	Manufacturer	Activation	Emission
Yellow 3	Azo	———	———	———
Blue 7	Anthraquinone	Geigy	300	350
Blue 120	Anthraquinone	Eastman	295	350
Red 60	Anthraquinone	———	———	———
Blue 3	Anthraquinone	Harshaw	290	———
Yellow 23	Diazo	Eastman	310	375
Yellow 54	Quinoline	duPont	240	350
Blue 56	Anthraquinone	duPont	230	340
Yellow 42	Sulfonamide	duPont	240	350

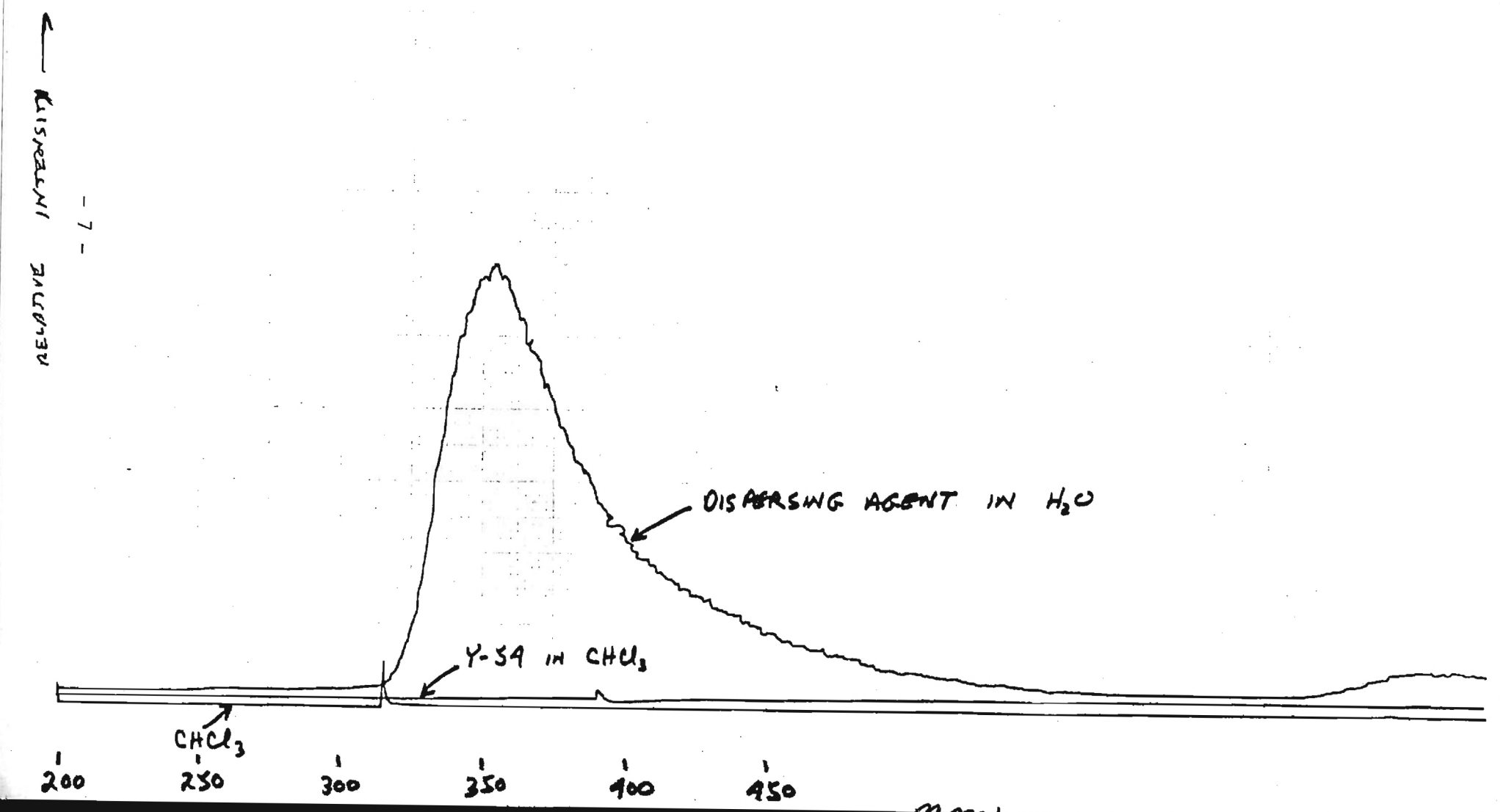
FIG. 2 — FLUORESCENCE SPECTRA OF SEPARATED DISPERSING AGENT AND PURE DISPERSE YELLOW 54.

TLC Separation & Extraction

DISPERSE YELLOW 54

ACTIVATION : 290 NM

EMISSION : 355 NM



Lignin sulfonates are the most commonly used materials as dispersing agents in disperse dyes. It appears probable that this material is present and persistent in carpet dye wastes. Authentic samples of lignin sulfonate dispersing agents are being obtained in an attempt to confirm this identification.

IV. Future Work

Studies are now underway on sampling procedures for use in analyses of streams containing carpet processing effluents.

E-27-626

Monthly Progress Report Number 7
(Feb. 15, 1975 - Mar. 15, 1975)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.

E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

Effort this month has been directed primarily toward development of sampling procedures for use in stream analyses for carpet processing chemicals.

II. Sampling Technique Development

The recovery of trace organic chemicals from waste water has been the subject of several recent studies. One of the more successful procedures has involved passing the waste water containing organic contaminants through columns of either activated carbon or ion exchange resins. The organic compounds adsorbed on the columns are then removed by backwashing with selected solvents. This procedure has a number of advantages - - a small sampling unit can be constructed for on-site collection over a long time period, it permits a several-fold concentration of the trace organic contaminants, and some preliminary separation of components is possible by judicious selection of backwashing solvents.

The effectiveness of both carbon black (Nuchar) and a recommended resin (Amberlite XAD-2) for removing anxiliary chemicals and dyes used in textile processing has been determined in several bench scale experiments. Standard solutions of several polyester dye carrier components (o-dichlorobenzene, 1-methylnaphthalene, trichlorobenzene, biphenyl, butyl benzoate) were prepared at concentrations less than 20 parts-per-million. The solutions were passed through approximately 1" columns of activated carbon or the resin in standard laboratory burettes (50 ml). Concentrations were determined by UV spectrophotometry using previously prepared standard curves.

Results for the five carrier components are shown in Table 1. These results suggest that carrier components can be readily removed from waste water by either carbon or XAD-2 resin.

Similar studies have been carried out on several important disperse dyes. A number of references in the literature have indicated that disperse dyes are very difficult to remove by adsorption techniques. Results of studies on seven disperse dyes are shown in Table 2. The results in Table 2 clearly show a wide variance in the ability of both carbon and XAD--2 to remove disperse dyes. During the course of these experiments it was noted that the disperse dyes which were in solution (Yellow 3, Blue 3, Yellow 23) were readily removed. The dyes which were in a collodial state (as evidenced by cloudiness of the solutions) were not effectively removed. This suggests that molecular dispersion of the dyes should improve removal efficiency. Experiments to test this hypothesis are now underway.

III. Future Work

In addition to continued studies on disperse dye removal from waste water, experiments on backwashing of both carbon and XAD-2 columns are now underway.

Table 1

Removal of Dye Carrier Components From Water

Carrier Component	Carbon ppm in	Carbon ppm out	Carbon % Removed	XAD-2 ppm in	XAD-2 ppm out	XAD-2 % Removed
o-dichlorobenzene	14.6	1.5	90 +	14.6	1.5	90 +
1-methylnaphthalene	8.8	0.5	95 +	8.8	0.1	99
trichlorobenzene	8.4	1.0	90 +	8.4	1.0	90 +
biphenyl	15.1	0.5	95 +	15.1	-	100
butyl benzoate	14.4	-	100	14.4	-	100

Table 2

Removal of Disperse Dyes From Water

Dye	Carbon			XAD-2		
	ppm in	ppm out	% Removal	ppm in	ppm out	% Removal
Disperse Yellow 3	7.7	0.1	99	7.7	0.0	100
Disperse Blue 120	6.2	1.9	69	6.2	2.4	62
Disperse Blue 7	7.8	3.7	53	7.9	4.1	48
Disperse Blue 3	6.4	1.3	80	6.4	1.1	83
Disperse Red 60	6.7	1.3	80	6.7	2.1	69
Disperse Yellow 23	7.5	1.6	80	7.5	1.7	77
Disperse Yellow 54	7.1	3.3	55	7.1	3.5	51

E-27-626

Monthly Report Number 8
March 15, 1975 - April 15, 1975

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

Work has continued this month on development of systmes of analysis for organic contaminants in streams carrying carpet dyeing wastes. A tentative system has been developed which shows promise for these analyses.

II. Status of Phase I

Data collection is essentially complete on Phase I of the project. Data on processing of 44 million pounds of nylon and 21 million pounds of polyester fiber have been obtained. This represents 8% of the nylon carpet and 30% of all the polyester carpet produced during the first six months of 1974. This data is now being evaluated and a preliminary report on the results will be available soon.

III. Development of Analysis Procedures

Attempts to remove disperse dyes from water by absorption on either carbon or Amberlite XAD-2 resin have previously been only partially successful. For many disperse dyes approximately 50% of the dye remains in the water. In an attempt to improve removal efficiencies, selected solvents have been added to the water to give greater dispersion of the dyes. Of the solvents studied N,N-dimethylformamide gave the greatest improvement in removal effeciency. Results of these studies for several disperse dyes are shown in Table 1. These results suggest that increasing the dispersion of the dye greatly improves the removal efficiency. Subsequent experiments have shown that less N,N - dimethylformamide can be used without reducing the removal efficiency.

Studies have also been conducted on removal of the dyes from the absorbant by backwashing with selected solvents. These studies were done

Table 1

Removal of Disperse Dyes from Water-DMF

Carbon Absorption

Dye	Water only			Water + DMF		
	ppm in	ppm out	% Removed	ppm in	ppm out	% Removed
Disperse Yellow 3	7.7	0.1	99	19.52	0	100
Disperse Yellow 54	7.1	3.3	55	18.26	2.74	85
Disperse Blue 7	7.8	3.7	53	17.41	0	100

XAD-2 Absorption

	Water only			Water + DMF		
	ppm in	ppm out	% Removed	ppm in	ppm out	% Removed
Disperse Yellow 3	7.7	0.0	100	-	-	-
Disperse Yellow 54	16.7	8.1	55	18.76	0.6	97
Disperse Blue 7	7.9	4.1	48	19.52	0.8	96

with both acid and disperse dyes absorbed on carbon and XAD-2. The resin with absorbed dye was placed in a Soxhlet extractor thimble and extracted with solvents at the boil.

It was not possible to remove dyes from carbon with any of the solvents (benzene, methanol, perchloroethylene, trichlorobenzene, chloroform, acetone, pyridine) used. Thus although carbon will remove dyes from the water - DMF solutions, recovery appears to be a major problem with this absorbant.

Similar studies have been carried out on dyes absorbed on XAD-2. A trial run with benezene removed all of the visible color on the XAD-2 column. Studies to determine if the removal is quantitative are now underway.

The experiments conducted thus far suggest that organic compounds in carpet dye waste can be concentrated by absorption on XAD-2 resin. The absorbed compounds can be removed by backwashing and separated by thin layer chromatography. The separated components can be removed from the plate and determined quantitatively by absorption spectroscopy, fluorescence spectroscopy or other instrumental procedures.

IV. Future Work

Data analysis for completion of Phase I and continued development of analytical procedures are planned for the next month.

E-27-626

Monthly Progress Report Number 9

(April 15, 1975 - May 15, 1975)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward analysis of the data collected as part of Phase I of the project. Data on dye consumption is essentially complete and work is now under way on chemical auxiliaries. We are continuing efforts on development of analytical techniques for Phase II.

II. Dye Usage in Carpet Dyeing

During the first six months of 1974 the carpet industry produced carpet from approximately 548,000,000 pounds of nylon yarn and 71,000,000 pounds of polyester yarn. This fiber was dyed in one of four basic processes - beck-dyeing, continuous dyeing, printing and yarn dyeing. Discussions with a number of carpet industry experts suggest that the nylon and polyester fiber was processed as shown in TABLE 1. The types of nylon and polyester fibers processed by companies surveyed in this study and the methods used for coloration are shown in TABLES 2 and 3. The quantities of the more important dyes used in processing the fiber are given in the second column of Table 4. The dyes listed in TABLE 4 account for over 75% of the dye used in coloration of the 64 million pounds of fiber in the data base.

TABLE 1

CARPET FIBER COLORATION

Jan-June 1974

NYLON

	1,000 Pounds	%	1,000 Pounds	%
Yarn Dyed	109,600	20	5,580	3
Continuous Dyed	164,400	30	167,400	90
Beck Dyed	191,800	35	13,020	7
Printed	82,200	15	-	-

TABLE 2

TYPES OF NYLON AND POLYESTER YARN

USED BY COMPANIES IN DATA BASE

Fiber Type	Pounds
Nylon (Reg., Deep Dye, Lt. Dye)	39,757,000
Nylon (Cationic Dyeable)	7,260,000
TOTAL NYLON	47,017,000
Polyester (Reg., Deep Dye)	13,708,000
Polyester (Cationic Dyeable)	3,702,000
TOTAL POLYESTER	17,410,000
TOTAL FIBER DATA BASE	64,427,000

TABLE 3

METHODS OF COLORATION USED BY

COMPANIES IN DATA BASE

Coloration Process	Pounds
Nylon (Beck Dyed)	31,662,000
Nylon (Continuous Dyed)	14,033,000
Nylon (Printed)	1,322,000
Polyester (Beck Dyed)	17,410,000
TOTAL FIBER PROCESSED	64,427,000

Projections of the total consumption of dyes of each type used during the first six months of 1974 are given in column 4 of Table 4. These values were obtained by multiplying the dye use, as reflected in the data base, by a factor which gives the ratio of the total quantity of fiber colored by a given process to the quantity of that fiber in the data base. For example the factor for Disperse yellow 3 is 6.07. Disperse yellow 3 is used in beck dyeing of nylon fiber. The quantity of nylon fiber beck dyed during the first six months of 1974 (Table 1) was 191,800,000 pounds. The quantity of nylon fiber beck dyed in the data base is 31,682,000 pounds. The factor for Disperse yellow 3 was obtained from the ratio:

$$f = \frac{191,800,000}{31,662,000} = 6.07$$

By similar calculations the factors for continuous dyeing (primarily liquid dyes), beck and continuous dyeing with acid dyes, etc. were obtained.

The data in TABLE 4 reflect the relatively few dyestuffs that are used in large quantities in the coloration of carpets. For example, only 10 dyes were used in larger than 100,000 pounds quantities. Data on purities and exhaustion of these dyes are almost complete.

TABLE 4

MAJOR DYESTUFFS USED IN CARPET DYEING

DYE	# USED DATA BASE	FACTOR TO PROJECT USE J-J1975	USE FIRST 6 MO. 1974
Disperse Yellow 3	96093	6.07	583,285
Acid Yellow 151 (L)	63970	7.06	451,628
Acid Orange 128 (L)	49450	7.06	349,117
Disperse Yellow 23	63687	4.08	259,843
Acid Yellow 19	33228	7.58	251.868
Acid Yellow 135 (L)	25000	7.06	176,500
Disperse Yellow 54	42887	4.08	174.979
Acid Red 337 (L)	23940	7.06	169,016
Acid Blue 25 (L)	18400	7.06	129,904
Disperse Red 60	31735	4.08	129,479
Disperse Blue 7	16287	6.07	98,862
Acid Red 151	16260	6.07	98,698
Disperse Red 55	15825	6.07	96,058
Acid Yellow 135	15085	6.07	91,566
Acid Red 151 (L)	12940	7.06	91,356
Disperse Blue 120	20340	4.08	82,987
Basic Yellow 15	7412	9.26	68.635
Acid Blue 40 (L)	7450	7.06	52,597
Basic Yellow 53	5529	9.26	51,199
Disperse Orange 59	11835	4.08	48,287
Acid Red 337	7180	6.07	43,583
Disperse Blue 26	5931	7.06	41,873
Disperse Orange 20	5610	7.06	39,607
Disperse Yellow 42	8224	4.08	33,534
Acid Blue 25	5492	6.07	33,336
Disperse Blue 56	6561	4.08	26,769

III. Chemical Auxiliaries

A list similar to Table 4 is now being prepared for chemical auxiliaries used in carpet processing.

IV. Future Work

During the next month major effort will be directed to preparations of a report on Phase I of the project.

E-27-626

Monthly Progress Report Number 10

(May 15, 1975 - June 15, 1975)

Identification and Quantification of Organic Contaminants from Textile Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-626

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward analyses in preparation of the Phase I final report. Work on chemical auxiliaries is essentially complete. Efforts are continuing on analytical method development for Phase II.

II. Anxiliary Usage in Carpet Dyeing

A number of anxiliary chemicals are used in dyeing of nylon and polyester carpet. These chemicals can be divided according to their function in the dye bath into the following groups:

pH control - chemicals used to adjust the pH of the dyebath, prescour, and afterscour to the desired level.

Scouring agents - chemicals added to remove identification tints and oils from fiber prior to dyeing and to remove excess surface dye from the fiber after dyeing. Agents used to strip dye from the carpet for redyeing have also been included in this group.

Carriers - these compounds are used in dyeing of polyester fiber to open up the structure and permit disperse dye to diffuse into the fiber.

Leveling agents - these chemicals improve the uniformity of the dyeing. Included in this group are compounds which permit dyeing with both acid and cationic dyes in the same bath (compatibilizers).

Antifoaming agents - added to reduce foam buildup during scouring and dyeing.

Chelating agents - used to maintain metals in solution.

Softeners, Antistatic agents - used in final rinse to give carpet pleasing "hand".

The quantities of auxiliaries used in dyeing fiber by the companies surveyed during the first six months of 1974 are given in Table 1.

As shown in Table 1 carriers represent by far the largest volume chemical auxiliary used in carpet processing (30%). Typical carrier compositions are shown in Table 2. In addition to these types a number of scatter rug manufacturers use chlorobenzene based carriers. These carriers are emulsified mixtures of tri-, di-, and monochlorobenzenes.

Table 1

Chemical Auxiliary Usage in the Carpet Industry

Fiber Material	Pounds used Jan. - June 1974
Polyester fiber processed	47,017,000
Nylon fiber processed	17,410,000
Total fiber	64,427,000
pH Controls Chemicals	
Monosodium phosphate	375,093
Trisodium phosphate	432,651
Acetic acid	454,008
Formic acid	1,000
Sodium Carbonate	45,200
Ammonium hydroxide	15,775
Sodium hydroxide	5,500
Ammonium acetate	2,500
Scouring Agents	
Sodium hydrosulfite	83,030
Sodium perborate	81,025
Sodium hypochlorite	5,760
Sodium peroxide	1,150
Zinc sulfoxylate formaldehyde	6,950
Detergents	327,379
Carriers	1,467,551
Leveling Agent	517,308

Antifoaming Agents	1,467,551
Chelating Agent	580,760
Softeners, Antistatic agents	38,288
Miscellaneous Chemical	
Sodium chloride	15,000
Total	4,619,223

Table 2

Typical Carrier Compositions

Type: Molten Biphenyl (80% active)

65% Biphenyl
15% butyl benzoate
20% emulsifier

Type: Liquid Biphenyl (80% active)

60% Biphenyl
25% α-methylnaphthalene
15% emulsifier

Type: Aromatic Blend (80% active)

20% Biphenyl
65% α-methylnaphthalene
15% emulsifier

Leveling agents, detergents, softeners, and antistatic agents are all either anionic, nonionic, amphoteric or cationic surfactants. Typical products are ethoxylated alcohols, ethoxylated nonylphenol, sodium naphthalene sulphonate, sodium dioctyl sulfosuccinate, disodium diphenyl-oxide disulfonate, sulfonated castor oil, ethoxalated amines, sodium laurel phosphate, and steramides. Many of these materials perform more than one function in the dyebath.

Two compounds are used principally as chelating agents - ethylenediaminetetracetic acid (sodium salt) and ethylenedi-aminepentacetic acid (sodium salt). The latter is preferred if iron is present in the water.

Several types of materials are being used as antifoaming agents. Previously silicone containing compositions were used for this purpose but the problems with flammability created by these materials has resulted in their elimination from carpet dyebaths. Mineral oil, 2-ethyl hexanol and steramides are now the principal products being used.

A more detailed breakdown of chemical types of anxiliaries is being prepared for the final report.

III. Analytical Method Development

Refinement of the resin absorption procedure for concentrating carpet dyeing wastes is underway. Greater than 90% recovery of processing chemicals and dyes has been demonstrated using this technique. Samples of carpet dye waste were obtained from a large carpet facility and are being analyzed using this concentration technique followed by thin layer chromatography and UV absorption spectroscopy.

E-27-626

Final Report

Part I

Chemical Use and Discharge in Carpet Piece Dyeing

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Prepared Under Contract No.
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for

Environmental Protection Division
Department of Natural Resources
State of Georgia

The preparation of this report was financed in part through a grant from the U.S. Environmental Protection Agency under provisions of Section 106 of the Federal Water Pollution Control Act Amendments of 1972.

September, 1975

Final Report

Chemical Use and Discharge in Carpet Piece Dyeing

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Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

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September, 1975

Summary

A detailed analysis of carpet production processes has been conducted to determine the identities and quantities of chemicals used and discharged by the carpet industry. Data have been obtained and analyzed on processing of 65 million pounds of carpet face yarn (48 million pounds of nylon and 17 million pounds of polyester). The data included quantities of dyes and auxiliary chemicals used in coloration and finishing of the carpets produced from the yarn. These data have been used to estimate chemical use by the carpet industry in 1974 and to project chemical usage in 1980.

Data on purity and exhaustion of various dyes and chemical auxiliaries have been obtained and used to estimate the quantities of chemicals of various types discharged by the carpet industry in 1974. The available toxicity data on these materials is also given.

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I. INTRODUCTION

A. Carpet Industry in Georgia

The tufted carpet industry is indigenous to the state of Georgia. Since its beginning in northwest Georgia in the late 1800's this industry has revolutionized the production and marketing of floor coverings in the United States [1]. The carpet industry has had a major impact on the economy of Georgia in the past 20 years and is expected to be one of the fastest growing segments of the state's economy in the next several years [2-3].

The tufted carpet and rug industry in Georgia accounted for approximately 60% of all soft floor coverings produced in the United States in 1972, the last year for which data are available. Value of shipments from Georgia carpet manufacturers was 1.73 billion dollars [4] compared to the total United States value of shipments of 2.94 billion dollars [5]. The distribution of the carpet industry among several Georgia counties is shown in Table 1 [4]. The concentration of the carpet industry in northwest Georgia is indicated by the fact that approximately 50% of all carpet production in the United States is located in 8 northwest Georgia counties (Whitfield, Bartow, Catoosa, Chattooga, Floyd, Gordon, Murray, Walker) [6].

The carpet industry is one of the major users of Georgia's water resources. It is conservatively estimated that approximately 20 gallons of water are required to process each pound of carpet (weight excluding latex and secondary backing) [6]. A total of 22 billion gallons were required for carpet processing in Georgia in 1974 (943,080,000 square yards x 2 pounds per square yard x 20 gallons per pound x 0.60). The major portion of

Table 1

Distribution of the Georgia Carpet Industry
(SIC CODE 227)

Area	No. of Plants	Value of Shipments (Million Dollars)	%
United States (Total)	-	2,937	100.0
State of Georgia	248	1,727	58.8
Whitfield County	128	738	25.1
Gordon County	36	175	6.0
Bartow County	21	147	5.0
Murray County	19	36	1.2
Gilmer County	5	21	0.7
Eight Northwest Georgia Counties +*	-	1,499	51.0

+ Whitfield, Bartow, Catoosa, Chattooga, Floyd, Gordon, Murray, Walker.

* Data from Georgia Economic Model which may be on slightly different basis than other data in the table [6].

this water is subsequently discharged containing large quantities of organic and inorganic chemicals used in the various carpet manufacturing steps. In many cases the identities and concentrations of the chemical species being discharged are not known and their possible effects on water quality cannot be evaluated.

B. Objective of the Study

The concentration of carpet manufacturing in the Coosa River basin has presented considerable concern to officials responsible for water quality in the state of Georgia. The Coosa and its tributaries serve as a source of water for a number of cities and towns in Georgia and the presence in these supplies of unknown quantities of various organic and inorganic compounds from carpet processing is a problem of major importance. The present study was therefore undertaken to determine the chemical structure and quantities of organic and inorganic compounds currently used and discharged by the carpet industry.

C. Plan of the Study

A number of different types of fibers and a variety of processes are employed in the production of carpets and rugs. This diversity creates difficult problems in an attempt to assemble quantitative information on chemical usage in the carpet industry. The problem is compounded by the fact that most processing chemicals are sold by trade name and carpet manufacturers frequently have little information on the chemical composition or concentration of the materials. The high degree of competition between the chemical suppliers for the carpet industry also reduces the availability of information on carpet processing chemicals.

In organizing the data collection for this study the following plan was adopted. First, detailed information on fiber types and poundages being processed into carpet were obtained. Second, similar data on the various processing steps for each type of fiber were assembled and the quantities of each type of fiber used in the different processing steps was determined. Finally the types and quantities of processing chemicals used in each processing step for each type fiber was determined.

This organization of the study is illustrated in Figure 1. The 4 most important types (95%) of fiber used in carpet production are listed in one column. The principal processes used for coloration of these fibers are shown in the horizontal row. A matrix is then generated showing which fibers are processed in each of the various processes.

Since producer coloration of fiber and yarn dyeing are generally not carried out by carpet manufacturers, these processes are not included in this study. Major emphasis has been placed on chemical consumption in beck dyeing, continuous dyeing, and printing of nylon and on beck dyeing of polyester. The very limited quantities of polyester being continuously dyed and small quantities of acrylic fiber being printed did not permit a detailed analysis of these processes.

Four major sources of information have been employed to obtain information on chemical usage in the processes selected for study. First, the available literature (technical publications, fiber manufacturer's processing recommendations, procedures recommended by chemical suppliers and dyestuff manufacturers) was searched to determine suggested chemical usage in various types of carpet processing. Second, interviews were conducted with a number

Figure 1

Example of Study Plan

COLORATION PROCESSES

Fiber Types	Colored By Fiber Producer	Dyed in Yarn Form	Beck Dyed	Continuous Dyed	Printed
Nylon	0	+	+	+	+
Polyester	0	+	+	-	0
Acrylics	+	+	0	0	-
Polypropylene	+	+	0	0	0

\+ Significant Quantities of Fiber Colored by Indicated Process

\- Small Quantities of Fiber Colored by Indicated Process

0 Process Not Used for Fiber Type

of knowlegable people in the carpet industry to determine the current practices and projected changes in carpet processing. Third, data on chemical usage and production for a six month period (January to June of 1974) were obtained from a number of selected carpet manufacturers to permit detailed calculations on quantities of chemicals and dyestuffs used in carpet coloration. Finally, some data (particularly on activity and exhaustion) were obtained by laboratory experiments at the Georgia Tech School of Textile Engineering. The way in which these various sources were utilized in developing the comprehensive chemical usage table are described in detail in succeeding sections.

II. CARPET PRODUCTION PROCESSES

Carpets are currently produced in the United States by a number of techniques (weaving, tufting, needle-punching, yarn implantation, knitting etc.). The quantities of carpet produced by each of these methods in 1974 are shown in Table 2 [7]. The dominance (>90%) of the tufting process is immediately apparant from these data. The relatively small volumes of carpet produced by other processes and the fact that these processes use primarily precolored yarns has limited the present study to tufted carpets.

A. Tufted Carpet Production

In the tufting of carpets, face yarns are "stitched" or "sewed" into a backing fabric leaving loops or tufts of yarn extending above the fabric. The loops may be cut to give cut pile styles or left intact for loop pile carpets. The face yarns may be any of several types of fiber and may be either continuous filament yarns or yarns produced from staple fibers by the usual textile carding, drawing, and spinning processes. The face yarns may

Table 2

Carpets Produced by Various Methods
in 1974

Product	Quantity (1,000 sq. yds.)	Value of Product Shipment ($1,000)
Woven	23,249	182,539
Tufted	866,000	3,043,194
Knitted	9,309	37,179
Needle Punched	37,131	54,021
Other	3,444	11,191
Total	939,133	3,328,844

have been previously colored either by the fiber producer or by dyeing the fiber in the staple or yarn form. A more common practice is to tuft white yarns in the carpet and later dye the carpet in the piece.

B. Piece Dyeing

Piece dyeing is generally carried out by one of three processes - beck dyeing, continuous dyeing, printing. In beck dyeing the carpet is placed in a large heated tank containing water, chemical auxiliaries are added (to control pH, wetting, rate of adsorption of the dye by the carpet, etc.), the bath heated to the boil and held at that temperature for approximately 1 hour with constant movement of the carpet through the bath. In some cases the carpet is scoured (washed) prior to the beck dyeing operations to remove yarn identification tints, tufting oils, and yarn finishes. In other cases these yarn additives are removed by the dyebath during the dyeing cycle. At the end of the dye cycle, additions of dyestuffs may be required to obtain the proper color or shade required for the carpet. After the dyeing cycle, the carpet is usually afterscoured to remove excess dye and dye that is not firmly attached to the fiber (necessary to ensure "fastness" properties of the carpet).

In continuous dyeing the carpet is first "wet-out" in a solution containing water and a surfactant. A dye solution is then uniformly applied to the face yarn and the carpet passed into a "steamer" to achieve adsorption and diffusion of the dye into the fiber. After the steamer the carpet passes through a series of wash bowls which rinse the carpet and remove unfixed dyes.

Printing is generally accomplished by applying a thick dye paste to the surface of the carpet in a desired pattern (by the use of a series of patterned screens or rolls) and then passing the carpet into a steamer to

fix the dye. Following fixation the carpet is rinsed to remove excess print paste. Carpet is generally foam backed (see below) prior to printing to ensure dimensional stability during the printing process.

C. Backing

Following dyeing, the tufts are locked in the primary backing fabric by applying an adhesive (usually a rubber latex) to the primary backing. This adhesive penetrates the tufts and secures them to the backing fabric. Before curing the latex, a second backing fabric (secondary backing) is applied to the back of the carpet and is also secured to the primary backing by the latex adhesive. The secondary backing is required to give the carpet dimensional stability. In some cases the secondary backing is replaced by a layer of foam. The foam backed or secondary backed carpet is then passed into an oven to cure the latex. From the curing oven the carpet is inspected, packaged and either shipped or warehoused.

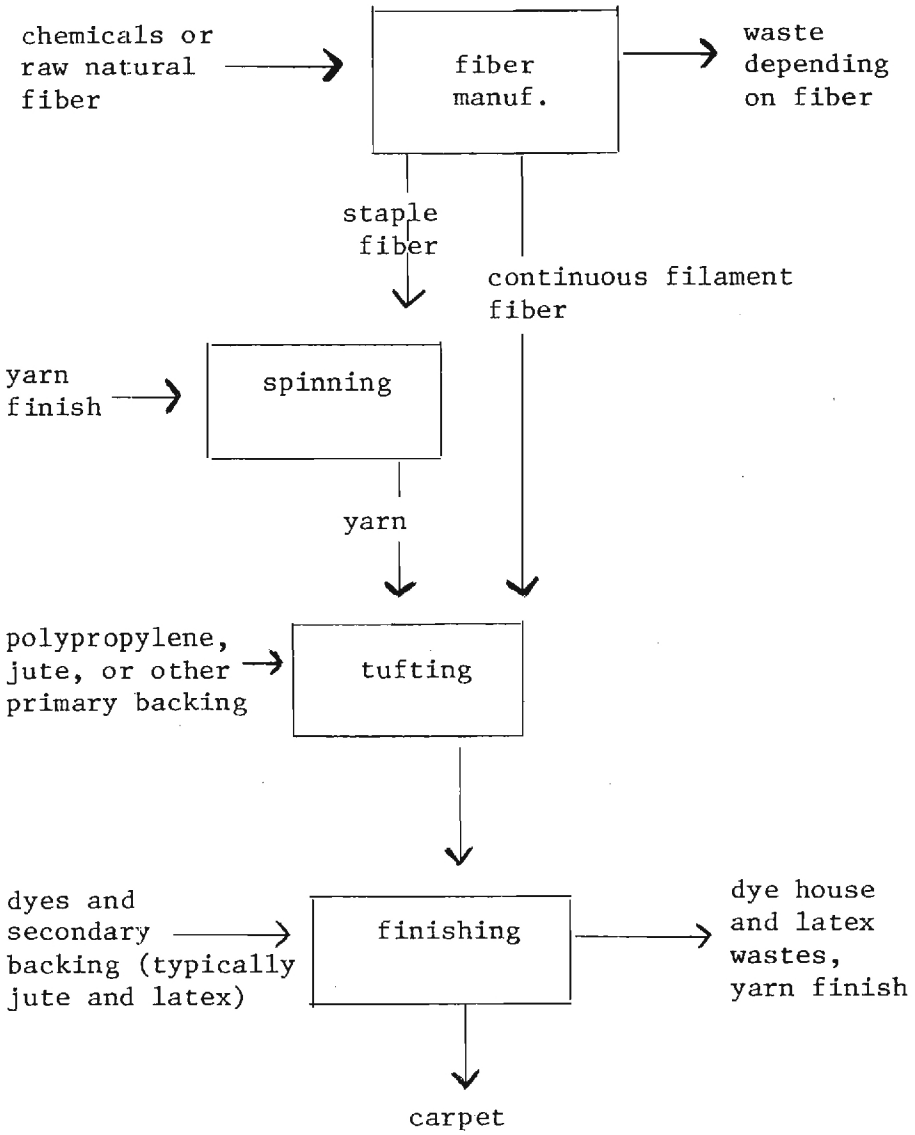
In the case of printed carpets a foam backing is usually applied prior to printing the carpet. This is significant in that the foam backing is subjected to steaming and washing steps during the printing operation that leaches a number of chemical species from the foam.

A schematic diagram of the carpet tufting process is shown in Figure 2 [6]. The material inputs and wastes involved in the various processing steps are indicated in Figure 2.

III. MATERIALS USED IN CARPET MANUFACTURE

A. Face Yarn

The types of fibers used as face yarn in carpet manufacturing during 1974 are given in Table 3. There is some variation in data on fiber use in



TUFTED CARPET MAKING PROCESS

FIGURE 2

Table 3

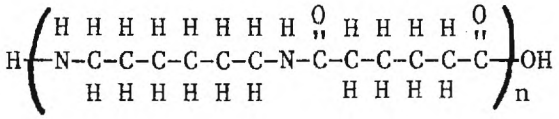
Fiber Usage in the Carpet Industry

1974 (1000 Pounds)

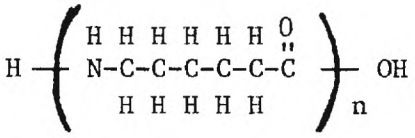
Fiber	First Quarter	Second Quarter	Third Quarter	Fourth Quarter	Total 1974	% of fiber used
Cotton	1212	1016	716	673	3617	0.3
Rayon	7569	6858	5532	4417	24376	1.8
Wool	6551	4934	4434	4151	20070	1.5
Nylon	244481	258677	239527	178182	920867	69.6
Acrylic/Modacrylic	34193	34465	31999	29202	124859	9.4
Polyester	43007	40538	39614	32844	156003	11.8
Polypropylene	21343	17209	19466	12674	70692	5.3
Other	790	740	892	532	2954	0.6
Total	359146	364437	342180	257675	1323438	

the carpet industry depending on the source and the method of computation. For example, data on fiber shipments to the carpet industry compiled by fiber manufacturing companies do not agree directly with Table 3. Likewise, estimates by knowledgeable industry representatives may also differ somewhat. Data in Table 3 were taken from Current Industrial Reports [7] published by the U.S. Department of Commerce. In all cases the data in Table 3 are the "revised" data published one quarter after the initial publication. Data in Table 3 were used in this study for all calculations involving quantities of fibers of various types used in carpet production during 1974. Nylon, clearly, is the major type of fiber used in carpet production with smaller quantities of polyester, acrylics, and polypropylene fibers accounting for a total of over 96% of all U.S. carpet production.

Two chemically different types of nylon are sold for carpet production. Nylon 6,6 is produced by polymerization of adipic acid with hexamethylene diamine and has the structure shown below



The second type, nylon 6, is produced by polymerization of caprolactam and has the structure

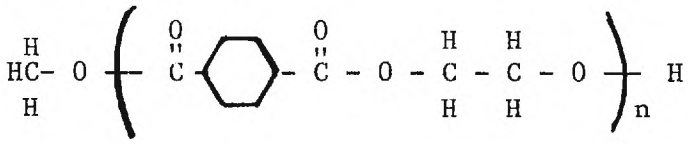


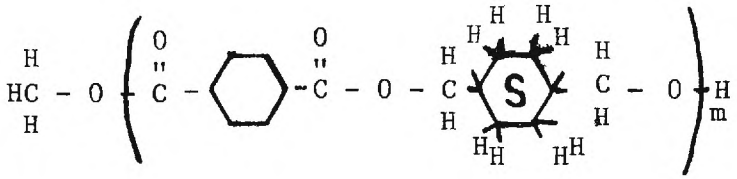
Unfortunately, a breakdown between 6 and 6,6 types used in carpet is not available. Informed industry estimates indicate that approximately 60% of the nylon fiber used is 6,6 type and 40% type 6.

In addition to the two major types of nylon, a number of fiber modifications with different dyeing characteristics are also available. These

variations either dye to a different level or with different types of dyes and are responsible for much of the styling latitude in current carpet manufacture. The common dyeing varients are regular dyeing nylon, light dyeing nylon, deep dyeing nylon, and cationic dyeable nylon. These types are produced either by incorporating selected comonomers in the polymer chain or by control of the number and kinds of end-groups present on the polymer chains. These dyeing variants require different kinds and concentration of dyes and auxiliary chemicals which had to be taken into account in this study.

Polyester fiber used in carpet production is also two principal types. The structures are shown below:





Polyester fiber is also marketed in regular, deepdye, and cationic dyeable modifications.

Finally, a number of organic species are present in the fiber as by-products of the polymerization reaction. Nylon 6 fiber contains approximately 1% of unreacted caprolactam. Nylon 6,6 and polyester fiber contain small quantities of compounds (called oligomers) which have the same chemical structure as the polymer but with 2 or 3 repeating units in a cyclic structure. Polyester may contain 1.0 - 3.0% of such oligomers and a

substantial quantity is removed from the fiber during the dyeing operation [8].

These fiber additives and impurities are a significant part of the organic waste resulting from carpet processing operations and have been considered in this study.

B. Backing Fabric

Materials used as primary backing fabrics for carpets have undergone a very significant change in the past few years. Woven jute, the traditional fabric for this purpose, has been largely replaced by synthetic polypropylene fabrics (either non-woven or woven slit film fabrics). This has made a major change in processing in that the separate dyeing step usually required for the jute primary fabric is no longer necessary. Data on primary backing fabrics is not yet available for 1974. In 1973, Jute accounted for 25% of the primary backing fabrics, polyolefin 71%, and cotton 4%. Based on usage trends, in 1974 polyolefins probably accounted for greater than 75% of this carpet raw material market. It is anticipated that jute will soon cease to be a factor in this market.

Primary backing materials generally have a lubricant added to the fabric to facilitate the insertion of the tufts without undue damage to the backing fabrics. It is estimated that at least 1%, by weight, of a lubricant [9] is added to the backing fabric. This lubricant is removed in the dyeing process.

Secondary backing fabrics are of little concern in the present study. These fabrics are added in the final finishing step and do not contribute to chemical usage or discharge.

C. Dyes and Chemical Auxiliaries

A very large number of different dyes and chemical auxiliaries are

used in dyeing of carpet. Typical dyeing recipes for various types of dyeing that are representative of the available literature data for nylon beck dyeing are shown in Table 4 [10-16]. In addition to dyes, 4 basic types of chemicals are used in dyeing of nylon with acid or disperse dyes - a sequestrant, a surfactant, a leveling agent and chemicals to control the dyebath pH. In dyeing of nylon containing cationic dyeable groups a compatibilizer* replaces both the surfactant and leveling agent and antifoam agents are recommended.

Typical dyeing recipes for beck dyeing of polyester fiber are given in Table 5. The major difference in polyester and nylon beck dyeing is the 5-10% carrier+ required in polyester dyeing. Polyester dyeing also frequently requires an afterscour to remove loose dye.

Dyeing formulations for the continuous dyeing of nylon carpet are shown in Table 6. The principal difference in continuous dyeing formulations is the use of natural gum thickeners as a viscosity modifier for the dye solutions. The dyeing assistants are also surfactant type materials but with some differences in structure from the types used as leveling agents or surfactants in beck dyeing.

Examples of carpet printing paste compositions are shown in Table 7. In addition to bean gums, print pastes require large quantities of benzyl alcohol and print aids ("screen release agents" or "defoamers") which are principally 2-ethyl hexanol.

A frequent last step in the dyeing of carpet is the application of a softener and/or antistatic/antisoiling finish to the carpet. These chemicals are applied in the final rinse before the carpet is backcoated.

* These materials are required to permit use of acid and basic dyes in the same bath.

+ By weight based on face yarn weight.

Table 4

Recipe Recommendations
For Nylon Beck Dyeing
(% on Carpet Weight)

	Component	Ref.10	Ref.11	Ref.12, 14,15	Ref.13	Ref.16
Prescour	Surfactant	0.02%		2.00%	0.12%	0.30%
	Oxidizing-Reducing Agent	4.00%		-	4.00%	3-4.00%
	pH Control	0.25%		2.00%	0.25%	2.00%
Dye Bath Acid Dyes	Sequestrant		0.25%	1.00%	0.25%	0.2-0.5%
	Surfactant		-	-	0.50%	-
	Leveling Agent		0.50%	2.00%	1.00%	X%
	pH Control		1.00%	1.00%	1.50%	4.80%
	Acid dyes		X%	X%	X%	0.2-0.5%
Dye Bath Disperse Dyes	Sequestrant		0.25%	0.50%		0.2-.5%
	Surfactant		0.50%	-		-
	Leveling Agent		0.25%	0.75%		X%
	pH Control		1.00%	2.00%		4.80%
	Disperse Dyes		X%	X%		X%
Dye Bath Multicolor	Sequestrant	-	0.25%	0.50%	-	0.2-0.5%
	Surfactant	-	-	-	-	-
	Compatibilizer	1.00%	1.00%	2.50%	1.00%	X%
	pH Control	0.30%	3.50%	1.00%	X%	1.50%
	Dye (Acid, Disperse, Cationic)	X%	X%	X%	X%	X%
	Antifoam Agent	0.20%	-	X%	X%	

Note: X% indicates that the quantity to be added depends on the particular color being dyed.

Table 5

Recipe Recommendations
For Polyester Beck Dyeing
(% On Carpet Weight)

	Component	Ref.17	Ref.11	Ref.18	Ref.19
Prescour	Surfactant	2.0%			1.0%
	pH control	2.0%			1.0%
Dyeing with Disperse Dyes	Carrier	8-12%	8-10%	5-10%	8-10%
	Antifoam Agent	0.5%	-	-	-
	Sequestrant	0.5%	0.25%	-	0.5-1.0%
	pH Control	2.0%	1.0%	1.0%	X%
	Surfactant	1.0%	.5-1%	1.0%	1.5%
	Dye	X%	X%	X%	X%
Dyeing with Disperse and Cationic Dyes	Carrier				5-10%
	Sequestrant				0.5%
	pH Control				10.50%
	Surfactant				0.5%
	Dye				X%
After Scour	Surfactant	1.5%			2.0%
	pH Control	1.5%			1.0%

Note: X% indicates that the quantity to be added depends on the particular color being dyed.

Table 6

Recommended Formulation for Continuous Dyeing
of Nylon Carpet
(% On Carpet Weight)

	Component	Ref.11	Ref.13	Ref.10	Ref.20
Wet-Out	Surfactant	0.3%	0.1-0.3%	0.1-0.3%	0.2-0.7%
	Sequestrant	-	0.5%	0.05%	-
Acid Dyes	Dyeing Assistant	1.2%	2.0%	0.1-0.5%	0.4-2.4%
	Gum Thickener	1.8%	0.6-1.2%	0.15-0.30%	0.8-2.4%
	Perservative *	0.8%	-	-	-
	pH Control	0.8%	0.2-0.8%	0.15-0.2%	0.04-0.0%
	Dye	X%	X%	X%	X%
Acid & Basic Dyes	Compatibilizer		0.8-2.0%	0.20-0.50%	0.8-4.0%
	Surfactant		0.4-1.2%	0.10-0.30%	0.20-2.0%
	pH Control		0.2%	0.10-0.15%	0.4-2.0%
	Thickener		0.6-1.2%	0.5-0.30%	0.8-2.4%
	Dye		X%	X%	X%
After Scour	Surfactant	0.2%			

* In current practice perservatives are not used

Note: X% indicates that the quantity added depends on the particular color being dyed.

Table 7

Print Paste Composition for Nylon Printing
(% On Carpet Weight)

Component	Ref. 11	Ref. 21
Wetting Agent	-	1.0%
Gum	2.5%	1.5%
Preservative*	1.0%	-
Print Aids	2.5%	2.0%
Benzyl alcohol	5.0%	3.0%
pH Control	2.5%	0.5-3.0%
Dyes	X%	0.6-.7%

* In current practice preservatives are not used.

D. Backing

The final processing step in carpet production is the application of the secondary backing. The material most frequently used as the secondary backing is woven jute. In 1973, 553 million square yards of jute were used in secondary backing of tufted carpet [22]. Sales of tufted roll goods for the same period were 807 million square yards (this figure excludes carpet used in transportation and scatter rugs which are backed by different procedures) [22]. Jute secondary backing, thus, accounted for approximately 70% of the backing for roll carpet.

Materials used in latex adhesives are shown in Table 8 [23]. Approximately 30 ounces of latex formulation per square yard (on a dry basis) are applied to the carpet. The secondary backing is then added and the latex cured in an oven.

An appreciable quantity of carpet is backed with foam rubber. In this type of construction a latex "precoat" is applied to bind the tufts to the primary backing and this is followed by application of the foamed backing latex. A formulation typical of the type used on printed carpets is given in Table 9 [24]. Table 9 also gives a typical formulation used for the "non-slip" backing used in many "scatter" rugs. These formulations are particularly significant in the present study due to the fact that printed carpets and scatter rugs are usually dyed and washed after the backing is applied. Chemicals used in the backing process, therefore, become a part of the waste stream.

E. Summary of Materials Usage

A summary of the classes of materials used in carpet production is given in Table 10. This table will serve as the basis for discussion of actual chemical usage in subsequent sections of the report.

Table 8

Typical Formulations For Carpet Latex (Dry Weight)

Carboxylated SBR Rubber*	100 parts
Silicone Antifoam	0.02 parts
Filler ∓	300 parts
Thickening Agent +	1.50 parts

*Contains SBR (Butodiene Styrene 60-40 to 40-60

1-2% Filler dispersing agent

1-2% Antioxidant

Usually marketed as a 50% total solids

Solids latex emulsion

+ Sodium Polyacrylate

∓ Either calcium carbonate or aluminum oxide, trihydrate.

Table 9

Typical Formulations Used in Foam Backed Carpets

Latex Precoat

	Parts dry
Latex	100
Sodium Hexameta Phosphate	1
Filler	450
Sodium Polyacrylate	1.5

Foam Latex Backings and Non-Slip Rug Backing

	Dry Parts by Weight	
	Foam	Non-Slip
Latex	100	100
Potassmm Oleate	3.5	2
Filler	100-400	100
Trimene Base	1-0	-
Zinc Diethyldithiocarbamate	2.5	0.75
Zinc Mercaptobenzothiazole	1.0	0,75
Sulfur	1.5	1.5
Zinc Oxide	4.0	3.0
Antioxidant	1.5	1.0
Potassium Hydroxide	0.2	-
Ammonium Acetate	1.5	-

Table 10

Summary of Classes of Materials Used
in Carpet Processing

I. Face Yarn

Yarn Finish
Polymerization Products (Monomer, oligomers)
Identification Tints

II. Primary Backing

Finish oils

III. Secondary Backing

IV. Dyeing

A. Beck Dyeing, Nylon
Acid, Disperse, Basic Dyes
Wetting Agents
Scouring Agents
Sequestrants
Leveling Agents
pH Control Agents
Compatibilizers
Antifoaming agents

B. Beck Dyeing, Polyester
Wetting Agents
Scouring Agents
Carriers
Sequestrants
pH Control Agents
Disperse Dyes

C. Printing, Nylon
Acid Dyes
Wetting Agents
Gum
Print Aids
Benzyl Alcohol
pH Control Agents

D. Continous Dyeing, Nylon
Acid, Basic Dyes
Gum
pH Control Agents
Compatibilizers
Leveling Agents

Table 10
(cont.)

V. Latex Backing

Latex
Filler
Antifoam Agents
Thickening Agents
Trimene Base
Zinc Diethyldithiocarbamate
Zinc Mercaptobenzothiazole
Sulfur
Zinc Oxide
Antioxidant
Potassium Hydroxide
Ammonium Acetate

IV. DATA ON CHEMICAL USAGE AND DISCHARGE

A. Fiber and Yarn Chemicals

As indicated previously, significant quantities of chemicals are present in and on the fibers and yarns used in carpet manufacturing which are removed by the dyeing and scouring procedures. These materials become a significant part of the waste discharged from carpet processing operations.

1. Finishes

Conversations with a number of experts in carpet fiber finishes indicate that approximately 0.5% finish is applied to carpet yarn by either the fiber manufacturer or the yarn spinner. The finish level of several samples of nylon 6,6 carpet yarn was determined in the laboratory by extraction and values from 0.33 to 0.72% were obtained with an average value of 0.62%. This is in good agreement with the anticipated 0.5% level suggested by finish experts. In the following calculations it will be assumed that 0.50% finish is removed from carpet yarn in the finishing and scouring processes.

Finishes used on carpet yarn are somewhat less complex than finishes used in other textile applications. Carpet yarn finishes are usually either a 2 or 3 component system with a small quantity of a perservative added to inhibit bacterial and fungus growth. The three components are lubricant, an emulsifier and an antistatic agent. The finish is prepared as a oil-in-water emulsion (10-20% active) and applied at a rate sufficient to give 0.5% active material on the fiber. A typical composition is shown below

50% lubricant

40% emulsifier

10% antistatic agent

0.1% perservative

In two component finishes the antistatic agent may be left out. The ratio of lubricant to emulsifier may also vary to account for differences in ease of emulsification of different lubricants.

Typical lubricants are sorbitan or glyceride esters of fatty acids obtained from vegetable oils (coconut oil, corn oil, peanut oil). Emulsified mineral oil blends are also used in some yarn lubricant formulations. Some typical chemical compositions for yarn lubricants are shown below

sorbitan monooleate

sorbitan monolaurate

polyethylene glycol oleates

white mineral oil

polyethylene glycol ethers

Emulsifying agents used in preparation of yarn finishes are usually highly ethoxylated species. Typical compounds used as emulsifying agents are shown below

polyoxyethylene sorbitan monolaurate

ethoxylated castor oil

ethoxylated aliphatic amines

triethanolamine oleate

Antistatic agents are generally quatenary ammonium compounds. Compounds which have been used for this purpose include [25]

soya dimethyl amino ethyl ethosulfate

N-cetyl-N-ethyl morpholinium ethosulfate.

The principal bacteriostat currently used in fiber finishes is believed to be 6-acetoxy-2,4-dimethyl methadioxane [25]. This compound was frequently mentioned by finish formulators as a preferred perservative for finish

compositions. It apparently has largely replaced the mercury containing compounds previously used.

An estimate of the quantity of these finish agents present in carpet processing effluents can be readily determined from the quantities of fiber used in carpet manufacturing in 1974. These estimates are shown in Table 11. No attempt has been made to separate the quantities of lubricants, emulsifiers and antistatic agents into the different types as this information is not available and the structures of the materials within a given group are similiar. The chemical species at the top of the lists shown are believed to be the more widely used materials in fiber finishes.

2. Polymerization By-products

The residual chemicals present in carpet fiber as a result of the polymerization process depend on the fiber type. Nylon 6 as polymerized contains up to 15 percent unreacted caprolactam monomer. Fiber manufacturers remove a major portion of this monomer for recycling in the polymerization process. The fiber as shipped to the carpet manufacturer still contains approximately 2% caprolactam and 0.4% cyclic oligomers which can be removed by boiling water [27]. Soxhlet extraction of a number of samples of Nylon 6 carpet yarns for 5 hours give 2.0 to 2.8% caprolactam and cyclic oligomers. Assuming that at least half of this material would be extracted in the dyebath, the 368,346,800 pounds of Nylon 6 (40% of 920,867,000 pounds of nylon) processed into carpet would be expected to contribute 3.7 million pounds of caprolactam and 1.5 million pounds of cyclic oligomers to carpet dye waste.

Polyester fiber is reported to contain from 1.3 to 3.8% of cyclic trimer and other oligomers [28]. These oligomers are known to extract in the carpet dye bath. Extraction experiments suggest that approximately 0.1% of these cyclic oligomers are removed by the dyeing cycle. Thus the 156 million pounds of polyester used in carpet manufacturing in 1974 contributed 156,000 pounds of

Table 11

Fiber and Yarn Chemicals Discharged From Processing
1.32 Billion Pounds of Face Yarn in 1974

Chemical Type	% on Fiber	Quantity Discharged (Pounds)
Finish, Lubricant	0.5 x 50	3,300,000
Finish, Emulsifier	0.5 x 40	2,640,000
Finish, Antistatic Agent	0.5 x 10	660,000
Finish, Preservative	0.5 x .1	6,600
Caprolactam	1.0	3,683,000
Polyester & Nylon Oligomers	0.1	760,000
Tints	0.05	160,000
Primary Backing Finish Oils	2.0	4,832,000

* 1.32 Billion pounds of fiber x 0.005 = weight of finish
weight of finish x 0.05 = pounds of lubricant

oligomers to the dye waste.

Linear monomers and other oligomers are also present in Nylon 6,6. Extraction experiments gave values of > 0.1% oligomers removed by hot water extraction. The 552,520,200 pounds of Nylon 6,6 (60% of 920,867,000 pounds) used in carpet manufacture in 1974 contributed > 550,000 pounds of oligomers to the dye waste.

3. Tints

Modified dyes which are very water soluble are used as identification tints on fibers with different dyeing characteristics. These tints are removed from the fiber either in prescouring or in the dye bath. Not all fiber has identification tints but based on the quantity of light, deep, and cationic dyeable nylon and deep dye and cationic dyeable polyester, it is estimated that 40% of the nylon and 20% of the polyester processed have such tints. The tint is added at approximately the 0.05% level (based on active dye). Tints therefore contributed approximately 160,000 pounds of waste to the carpet processing effluents in 1974.

Tints are standard dyes which have been modified to increase their water solubility. The modification usually involves reaction of one of the dye intermediates with the order of 8 moles of ethylene oxide. The quantity of tints used in 1974 is also given in Table 11.

4. Primary Backing Finish

All primary backing fabric contains a finish to assist in reduction of fabric damage and to reduce wear on tufting needles. These finishes are similiar to those used as yarn lubricants in Table 11. Emulsified mineral oil compositions are frequently used in this application. Primary backing fabrics contain approximately 2%* finish oils and these are also extracted in

* See Appendix C

the dye bath. The following quantities of primary backing fabrics were used in carpet production in 1974 [7]

Jute 214,540,000 square yards

Polypropylene 564,485,000 square yards

Cotton 15,193,000 square yards

Other 4,094,000 square yards

Assuming that cotton and jute fabrics weigh 7 oz. per square yard and polypropylene fabrics 4 oz. per square yard, the weight of finish oils used in 1974 (at the 2% level) is 2.4 million pounds. These finish oils also contribute to the waste from carpet processing.

5. Secondary Backing Fabrics

As indicated previously secondary backing fabrics do not contribute significantly to carpet processing wastes. However some carpet has a foam secondary backing which in the case of printed carpets can contribute to carpet processing effluents. This contribution will be considered in the section on printed carpets.

B. Dyes and Dyeing Chemicals

To estimate chemical use and discharge for the various coloration processes used in carpet production, it is necessary to have an accurate estimate of the quantities of carpet which are colored by the various processes. This information is not readily available in the published literature. In order to obtain such an estimate for 1974, interviews were conducted with a number of people familiar with carpet production. These responses were used to estimate the quantities of polyester and nylon carpet which are colored by various processes. These estimates are shown in Table 12. They are believed to be accurate to within $\pm$ 3%.

Table 12

Carpet Produced by Various Coloration Processes in 1974

		Yarn Dyed	Beck Dyed	Continuous Dyed	Printed	Total
Nylon	%	20	35	30	15	100
	1000 Pounds	184,173	322,304	276,260	138,130	920,867
Polyester	%	3	90	7	-	100
	1000 Pounds	4,680	140,403	10,920	-	156,003

In the subsequent analysis of the chemical use and discharge in dyeing, yarn dyeing will not be treated as this has traditionally been carried out by either fiber manufacturers or suppliers to the carpet industry. The very small volume of polyester fiber which is continuously dyed has not permitted sufficient data to be collected on this process to be meaningful. Chemical use and discharge has been limited, therefore, to beck dyeing, continuous dyeing, and printing of nylon and beck dyeing of polyester. These processes accounted for over 90% of all polyester carpet and 80% of all nylon carpet produced in the United States. The almost exclusive use of producer coloration or other yarn dyeing techniques for the other fibers widely used in carpets (acrylic, polypropylene, wool) has resulted in very little coloration of carpets from these fibers by the carpet manufacturers.

To determine the chemical usage in current carpet coloration processes, actual production records were obtained from a number of carpet companies. The information requested is shown in Table 13. Data were obtained from six carpet manufacturing facilities including both large and small firms. Data on all three major types (beck dyeing, continuous dyeing, printing) of carpet coloration processes were a part of the data base. Data were obtained on processing of over 65 million pounds of carpet face yarn including 48 million pounds of nylon and 17 million pounds of polyester fiber.

Due to the very sensitive nature of this data taken from company production records, no breakdown of data by individual company will be given. All data presented in this report is a composite of data collected from all 6 carpet processing facilities. A comparisom of the data base with total fiber processed into carpet during 1974 is given in Table 14. As indicated in Table 14 the data base represents at least 5% of all carpet processed in 1974 in each category with the exception of nylon printing. It was felt

Table 13

Data Obtained From Carpet Conpanies
on Carpet Coloration Processes

I. Pounds of fiber (face yarn weight) wet-processed January 1 to June 30, 1975.

A. Pounds of Polyester Fiber

1. Pounds of Polyester fiber regular dye
2. Pounds of Polyester fiber deep dye
3. Pounds of Polyester fiber cationic dye

B. Pounds of Nylon Fiber

1. Pounds of Nylon fiber light dye
2. Pounds of Nylon fiber regular dye
3. Pounds of Nylon fiber deep dye
4. Pounds of Nylon fiber cationic dye

C. Pounds of Acrylic Fiber

D. Pounds of Wool

E. Pounds of Polypropylene

II. Pounds of Fiber Processed by Various Methods

A. Pounds of Fiber Yarn or Stock Dyed
B. Pounds of Fiber Beck Dyed
C. Pounds of Fiber Printed
D. Pounds of Fiber Continuous Dyed

III. Pounds of Dyestuff Used by Each Kind by Maunfacturer or by C.I Number (For Example: Artisil Yellow G, C.I. Disperse Yellow 3)

IV. Pounds of Each Type of Chemical Auxiliary (Wetting Agents, Leveling Agents, Thickeners, pH Control Agents, etc.) Used in Processing the Fiber Given in I above.

V. Pounds of Jute Primary Backing Dyed During January 1 to June 30, 1974.

VI. Pounds of Carpet Latex Backed, Pounds of Carpet Foam Backed and Pounds of Chemicals of Each Type Used in These Processes.

that this data base could be used for extrapolation to total chemical usage in 1974 with a high degree of confidence.

A breakdown of nylon and polyester yarn by dyeing type from the data base is given in Table 15. This data is important since different dyeing procedures are used in production of carpets containing cationically dyeable fiber.

1. Dyestuff Used in Carpet Coloration

A total of 811,109 pounds of dye were used in coloration of the 65,582,000 pounds of carpet in the data base. Processing of each pound of fiber required on the average .0124 pounds of dye (1.24%). This number is larger than expected due to the large quantity of liquid dyes used (see below). A detailed breakdown of the 30 most commonly used dyes is given in Table 14A. The dyes shown in Table 14A accounted for over 83% of all dyes used in carpet coloration by companies in the data base.

The liquid dyes presented some problems in that they are regular powder dyes which are already dispersed in water by the dye manufacturer. In order to determine the amount of solids in these liquid dyes, samples were evaporated to dryness in a laboratory Rotovap unit. The per cent solids was then calculated by weight. Results for the liquid dyes are shown below

Acid Yellow 151	20%
Acid Orange 128	20%
Acid Yellow 135	40%
Acid Blue 25	30%
Acid Red 151	40%

Values used for Acid Red 337, Acid Blue 40, Basic Yellow 53 and Acid Red 266 were estimated from information supplied by carpet dyers.

Table 14

A Comparison of the Data Base With
Carpet Production During 1974

Fiber Processed in 1974	Total (1000 Pounds)	Data Base (1000 Pounds)	Data Base % of Total
Nylon, Total	920,867	48,172	5.2
Beck Dyed (35%)	322,304	31,662	9.8
Continuous Dyed (30%)	276,260	14,033	5.1
Printed (15%)	138,130	2,477	1.8
Yarn Dyed (20%)	184,173	-	-
Polyester, Total	156,003	17,410	11.2
Beck Dyed (90%)	140,403	17,410	12.4
Continuous Dyed (7%)	10,920	-	-
Yarn Dyed (3%)	4,680	-	-
Fiber, Total All Types	1,323,438	65,582	5.0

Table 14A

Dyeing Variants of Nylon and Polyester Yarn Processed by Companies in Data Base

Fiber Type	Quantity Processed (1000 Pounds)	%
Nylon (Regular, Deep, Light Dye)	40,912	84.9
Nylon (Cationic Dyeable)	7,260	15.1
Total Nylon	48,172	100.0
Polyester (Regular, Deep Dye)	13,708	78.7
Polyester (Cationic Dyeable)	3,702	21.3
Total Polyester	17,410	100.0

Table 15

Major Dyes Used In Carpet Coloration

Rank	Dye	Pounds Powder	Pounds Liquid	Adjusted Total Pounds	Use ♯	Factor +	Quantity Used in Pounds
1	Disperse Yellow 3	96093	-	96093	N,b	10.18	978227
2	Disperse Yellow 23	63687	-	63687	P,b	8.06	513317
3	Acid Yellow 19	33228	-	33228	N,bc	13.10	435287
4	Acid Yellow 151	6022	63970	18816	N,cp	(P)25.10(L)19.69	403066
5	Acid Yellow 135	15085	25000	25085	N,bc	(P)13.10(L)19.69	394514
6	Disperse Yellow 54	42887	-	42887	P,b	8.06	345669
7	Acid Red 151	16260	12940	21436	N,bc	(P)13.10(L)19.69	314921
8	Acid Red 337	7180	23940	16756	N,bc	(P)13.10(L)19.69	282609
9	Disperse Red 60	31735	-	31735	P,b	8.06	255784
10	Acid Orange 128	1350	49450	11240	N,c	19.69	221316
11	Disperse Blue 7*	16287	-	16287	N,b	10.18	165802
12	Disperse Blue 120	20340	-	20340	P,b	8.06	163940
13	Disperse Red 55	15825	-	15825	N,b	10.18	161099
14	Acid Blue 40	4650	7450	7630	N,bcp	15.29	116663
15	Acid Blue 25	5492	18400	11012	N,bc	(P)13.10(L)19.69	108689
16	Erionyl Orange 3G (Acid Or.)	5275	-	5275	N,c	19.69	103865
17	Acid Red 266	3015	5585	5249	N,c	19.69	103353
18	Disperse Orange 59	11835	-	11835	P,b	8.06	95390
19	Basic Yellow 53	5529	4280	7669	C,bc	9.47	72625
20	Basic Yellow 15	7412	-	7412	C,b	9.47	70192
21	Stylacyl Red RY (Acid Red)	6660	-	6660	N,b	10.18	67799
22	Disperse Yellow 42	8224	-	8224	P,b	8.06	66285
23	Acid Yellow 198	4634	-	4634	N,bc	13.10	60705
24	Disperse Blue 26	5931	-	5931	N,b	10.18	60378
25	Disperse Orange 20	5610	-	5610	N,b	10.18	57110
26	Disperse Blue 56	6561	-	6561	P,b	8.06	52882
27	Artisil Red 36 (Disp. Red)	5227	-	5227	P,b	8.06	42130
28	Acid Yellow 38	4097	-	3097	N,b	10.18	41707
29	Basic Yellow 50	4355	-	4355	C,b	9.47	41242
30	Basic Yellow 11	3874	-	3874	C,b	9.47	36687
	Total Dye (Pounds)	464360	211015	524670	-	-	5,833,253

♯ N-Nylon, P-Polyester, b-beck, c-continous, p-printing

* Sold as a major component in mixtures of dyes for nylon carpet coloration

+ (P) and (L) indicate factors for powder and liquid dyes

In order to obtain an estimate of total dye consumption during 1974 it is necessary to modify the quantities of dyes shown in Table 15 by a factor accounting for the different dyeing procedures in which the dye is commonly used. For example the data base has a higher percentage of data from polyester dyeing than from nylon dyeing. A larger multiplication factor is therefore required for dyes used in nylon dyeing than is required for polyester dyes. In Table 15 the ways in which the various dyes are employed is shown in column 6. In general polyester is dyed with disperse dyes, nylon with both disperse and acid dyes on the beck and with acid dyes only in continuous dyeing and printing, and basic dyes are used with both nylon and polyester cationic dyeable fiber. The factors used in Table 15 were calculated by the following procedures:

Nylon, beck dyeing, disperse dyes

$$\frac{\text{Nylon, total pounds beck dyed in 1974}}{\text{Nylon, pounds beck dyed, data base}} = \frac{322,304}{31,662} = 10.18$$

Polyester, beck dyeing, disperse dyes

$$\frac{\text{Polyester, total pounds beck dyed in 1974}}{\text{Polyester, pounds beck dyed, data base}} = \frac{140,403}{17,410} = 8.06$$

Nylon, continuous dyed with acid dyes (liquid & powder)

$$\frac{\text{Nylon, total pounds continuous dyed in 1974}}{\text{Nylon, pounds continuous dyed, data base}} = \frac{276,260}{14,033} = 19.69$$

Nylon, continuous and beck dyed, acid dyes

$$\frac{\text{Nylon, total pounds countinuous and beck dyed in 1974}}{\text{Nylon, pounds continuous and beck dyed, data base}} = \frac{598,564}{45,695} = 13.10$$

Nylon, continuous, and beck dyed and printed, acid dyes

$$\frac{\text{Nylon, total pounds continuous, beck dyed, printed in 1974}}{\text{Nylon, pounds continuous, beck dyed, printed, data base}} = \frac{736,694}{48,172} = 15.29$$

Nylon, continuous dyed and printed, acid dyes

$$\frac{\text{Nylon, total pounds continuous dyed and printed in 1974}}{\text{Nylon, pounds continuous dyed and printed, data base}} = \frac{414,390}{16,510} = 25.10$$

Cationic dyeable fiber, basic dyes

$$\frac{\text{Cationic fiber, estimated* total pounds dyed in 1974}}{\text{Cationic fiber, pounds dyed, data base}} = \frac{103,825}{10,962} = 9.47$$

*Estimated 15% of nylon beck and continuous dyed (89,785) and 10% of polyester beck dyed (14,000) is cationic dyeable type.

All factors above are calculated from the pounds (in 1000's) of fiber processed by the various techniques divided by the pounds (in 1000's) of fiber processed by the same techniques in the data base. Some dyes used only for printing do not appear in Table 15 due to the fact that even when the printing factor (55) is taken into account, the total quantities of these dyes used is less than those shown in Table 15.

The total quantity of dye used in 1974 can be obtained by multiplying the total estimated consumption of the 30 dyes in Table 15 by 1.25 (to account for the fact that these 30 dyes represent 80% of all dye used). Total dye consumption for piece dyeing of carpet in 1974 was approximately, therefore, 7.3 million pounds or about 0.8% based on weight of fiber piece dyed (from Table 14). This figure is in excellent agreement with expected values based on current dyeing practice.

Dyes as sold by the manufacturer are almost never pure dye. They contain impurities from dye manufacture, dispersing agents to assist in preparing the dye for use, and diluents to control the strength of the dye from batch to batch. The per cent pure dye has been determined for a number of the dyes

shown in Table 15. For disperse dyes, a sample of the dye as sold was placed in the thimble of a soxhlet extractor and extracted with benzene for 48 hours. The dye is soluble in benzene but other materials present are not. A plot of absorbance versus concentration of the pure dye is compared with a similar curve for the dye as sold. The ratio of the slopes of these curves gives the percent purity. Similar techniques are used for acid dyes except that the pure dye is obtained by repeated recrystallization from methanol.

Results of the purity studies on several disperse dyes are shown below

Disperse Yellow 23	19%
Disperse Yellow 54	25%
Disperse Red 60	16%
Disperse Blue 120	12%
Disperse Orange 59	31%

These data are in good agreement with statements of disperse dye manufacturers that disperse dyes are rarely more than 40% pure dye with most disperse dyes between 20 and 25% pure dye. Since the purity will vary from manufacturer to manufacturer an average value of 22% was assumed for disperse dyes.

Acid dyes are traditionally somewhat purer than disperse dyes. Acid dyes used in carpet processing are approximately 50% pure and this value was used in calculation of quantity of pure dye used in carpet coloration.

A small portion of the dye remains in the dyebath at the completion of the dye cycle and is discharged with the spent dyebath. Studies on the quantity of dye removal from the bath during the dye cycle have been made on a number of carpet dyes. In these studies small carpet samples were

dyed in the laboratory under conditions similiar to those employed in commercial dyeing. The quantities of dye in the bath before and after the dye cycle were determined spectrophotometrically using standard curves prepared using commercial dyes. Results for a number of dyes are shown below:

Dye	% Exhaustion
Disperse Yellow 3	91
Disperse Blue 7	96
Disperse Yellow 23	60
Disperse Yellow 42	71
Disperse Orange 59	72
Disperse Yellow 54	89
Disperse Red 55	90
Disperse Red 60	89
Disperse Blue 120	85
Acid Yellow 38	92
Acid Yellow 19	95
Acid Yellow 151	98

These values represent maximum exhaustion values under carefully controlled laboratory conditions. In actual practice somewhat larger quantities of dyes are undoubtedly left in the dye bath. Average values of 92% for disperse dyes on nylon, 78% for disperse dyes on polyester and 95% for acid dyes on nylon were used in calculations of dye discharge.

Based on usage, purity and exhaustion data, the quantities of various dyestuffs present in water discharged from carpet processing operations have been calculated and are given in Table 16. Structures of the more important

Table 16

Quantities of Dye Discharged in Carpet Piece Dyeing Waste Water in 1974

Dye	Quantity Used in 1974 (Pounds)	Purity %	Exhaustion %	Quantity Discharged in 1974 (Pounds)
Disperse Yellow 3	978227	22	92	17,217
Disperse Yellow 23	513317	22	78	24,845
Acid Yellow 19	435287	50	95	10,882*
Acid Yellow 151	403066	50	95	10,077*
Acid Yellow 135	394514	50	95	9,863*
Disperse Yellow 54	345669	22	78	16,730
Acid Red 151	314921	50	95	7,873*
Acid Red 337	282609	50	95	7,065*
Disperse Red 60	255784	22	78	12,380
Acid Orange 128	221316	50	95	5,533*
Disperse Blue 7	165802	22	92	2,918
Disperse Blue 120	163940	22	78	7,935
Disperse Red 55	161099	22	92	2,835
Acid Blue 40	116663	50	95	2,917*
Acid Blue 25	108689	50	95	2,717*
Erlonyl Orange 3G (Acid Or.)	103865	50	95	2,597*
Acid Red 266	103353	50	95	2,584*
Disperse Orange 59	95390	22	78	4,617
Basic Yellow 53	72625	50	95	1,816*
Basic Yellow 15	70192	50	95	1,755
Stylacyl Red RY (Acid Red)	67799	50	95	1,695
Disperse Yellow 42	66285	22	78	3,208
Acid Yellow 198	60705	50	95	1,518*
Disperse Blue 26	60378	22	92	1,063
Disperse Orange 20	57110	22	92	1,005
Disperse Blue 56	52882	22	98	2,559
Artisil Red 3G (Disp. Red)	42130	22	78	2,039
Acid Yellow 38	41707	50	95	1,043
Basic Yellow 50	41242	50	95	1,031
Basic Yellow 11	36687	50	95	917
Total Dye	5,833,253			171,234

* See discussions in Section IV-D

dyes (where available) are shown in Appendix A.

The diluents present in commercial dyes are equally, if not more important, in contributing to chemical discharge. The most common materials used as diluents in dyes are sugar, dextrin , salt, sodium sulfate, lignin sulfonate (Marsperse N, Reax 85A and naphthalene sulfonate (Tamol N or SN). Unlike the dye, which is primarily removed by the carpet from the bath, the diluents are very water soluble and are discharged with the spent dye bath. Most of the diluents used with acid dyes are either readily biodegradable organics (sugars, dextrin etc.) or inorganic salts. Lignin sulphonate is a frequently used diluent in disperse dyes. From the data base it is estimated that 3.3 million pounds of disperse dye were used in carpet production in 1974 (139,746 pounds x 10.18 for nylon plus 38,191 pounds x 8.06 for polyester or 46% of all dye used). Assuming that on the average disperse dyes contain 40% lignin sulphonate as a diluent and dispersing agent, a total of 1.3 million pounds of these materials were discharged in 1974. Lignin sulphonate can be detected in all streams carrying waste from carpet dyeing operations in Georgia (fluorescence peak at 350 nm) [29]. Data on structure of commonly used lignin sulphonate used as dye diluents and dispersing agents are given in Appendix A.

2. Chemical Auxiliaries used in Carpet Coloration

In addition to dyes, a number of other chemical species are used in dye baths and print pastes to assist in the dyeing process. These assistants perform a number of functions in the dye bath:

pH Control Agents - used to control the pH at level required for the particular dyeing process

Sequestrants - frequently required to complex metal ions and prevent their deposit in the dye beck or interaction with dyes

Surfactants - used for many different purposes including wetting agents to enhance wetting of the carpet, detergents to assist in removal of dirt and finish oils, leveling agents to improve the uniformity of the dyeing, compatibilizers to permit dyeing with acid and basic dyes in the same bath, retarders to reduce the rate of initial dye adsorption, antistatic agents, softeners, and lubricants to enhance the hand and end-use performance of the carpet, and antifoaming agents (of the non-silicone type). A given surfactant species may perform multiple functions in the dye bath.

Scouring Agents - primarily inorganic oxidizing and reducing agents used to remove identification tints and excess surface dye from the carpet

Carriers - compounds which open up the structure of polyester fiber to permit dye diffusion into the fiber

Thickeners - primarily gums used to control the viscosity of print pastes and continuous dye liquor

The quantities of these chemical used by companies in the data base are given in Table 17 for beck dyeing, and continuous dyeing.

The chemicals used for dyebath pH control are used in all processing techniques. Factors for estimating total use therefore were determined by multiplying the data base use times the total fiber processed in beck and continuous dyeing in 1974 (738,967,000) divided by the fibers processed by these techniques in the data base (63,105,000). A similar factor was used for sequestrants, wetting agents, detergents, antifoaming agents and softners, antisoil and antistatic agents. Since scouring agents are more commonly used in pre-and after scouring in beck dyeing, the factor for these agents was determined by multiplying the data base value by the pounds of carpet beck dyed in 1974 (462,003,000) divided by the pounds beck dyed in the data base (49,072,000). The same factor was used for sodium chloride. The factor for leveling agents was determined from the ratio of

Table 17

Chemical Auxiliaries Used in Carpet Beck and Continuous Dyeing by Companies in Data Base and Estimated Total 1974 Use and Discharge

Chemical Type	Pounds Used (Data Base)	Factor	Total Industry Use in 1974 (Pounds)	% Active Components	% Exhaustion	1000's Pounds Discharged in 1974
pH Control Agents						
Monosodium Phosphate	290,619	11.71	3,403,148	100	0	3,403
Tri&Tetra Sodium Phosphates	432,651	11.71	5,066,343	100	0	5,066
Acetic Acid	322,790	11.71	3,779,871	100	0	2,117
Formic Acid	118,167	11.71	1,383,736	100	0	1,204
Sodium Carbonate	45,200	11.71	529,292	100	0	529
Ammonium Hydroxide	15,775	11.71	184,725	100	0	92
Sodium Hydroxide	5,500	11.71	64,405	100	0	64
Ammonium Acetate	2,500	11.71	32,788	100	0	33
Ammonium Sulfate	78,948	11.71	924,481	100	0	924
Diammoniam Hyd. Phosphate	5,526	11.71	64,709	100	0	65
Scouring Agents						
Sodium Hydrosulfate	650,039	9.43	613,318	100	Reacts	-
Sodium Perborate	99,016	9.43	933,721	100	Reacts	-
Sodium Peroxide	1,150	9.43	10,845	100	Reacts	-
Sodium Hypochlorite	5,760	9.43	54,317	5.25	Reacts	-
Zinc Sulfoxylate Formaldehyde	6,950	9.43	65,539	100	Reacts	-
Sequestrants	38,288	11.71	448,352	50	0	224
Surfactants						
Wetting Agents, Detergents	316,573	11.71	3,707,070	50	0	1,354
Leveling Agents	326,252	13.10	4,274,901	50	0	2,137
Compatibilizers	191,060	9.47	1,809,338	50	0	905
Antifoaming Agents	530,472	11.71	6,211,827	100	15	5,280
Softeners, Antisoil, Anti-Stat.	163,295	11.71	1,912,184	50	95	48
Carriers	1,467,551	8.06	11,828,461	100	0	11,828
Thickeners	117,333	19.69	2,310,287	100	0	2,310
Misc. Chemicals						
Sodium Chloride	15,000	9.43	141,450	100	0	141
Silicone type Antifoaming Agent	25,073	19.69	493,687	5	0	25

the total quantities of nylon continuous and beck dyed in 1974 and in the data base. Similarly the factors for carrier use were determined from the polyester fiber use and the factor for thickners and silicone type antifoaming agents from the ratio of the quantity of fiber continuously dyed in 1974 to the quantity continuously dyed in the data base. The factor for compatibilizers was determined from the quantities of cationic dyeable fiber processed in 1974 divided by the quantity of this type fiber in the data base.

The pH control agents and scouring agents are identified in Table 17.

The two most commonly used sequestrants are ethylenediaminetetra acetic acid, tetrasodium salt and diethylenetriaminepentaacetic acid, pentasodium salt. The latter is desirable where iron must be complexed in the dye bath. Structures are shown in Appendix B.

The most commonly used carriers* in carpet dyeing at the present time are mixtures of components. Analyses in laboratories at the Georgia Institute of Technology (gas chromatography, infrared spectroscopy, and nuclear magnetic resonance spectroscopy) gave the same three major components in two widely used carriers. Results of the analysis are indicated below

	Carrier	
	A	C
Biphenyl	36%	50%
Methyl benzoate	36%	20%
Naphthalene	23%	15%
Emulsifier	5%	15%

The above compositions are representative of the most of the carriers used in carpet dyeing. There are reports of trichlorobenzenes being used in some "scatter" rug dyeing [30] but the practice is not widespread and

* Carriers swell or open up the fiber structure so dyes can diffuse into the fiber.

could not be confirmed in this study. Trichlorobenzene based carriers are used in some yarn dyeing operations where completely enclosed equipment is employed in the dyeing operation.

The principal thickener used in continuous dyeing is a modified glactomannan derived from the guar plant. This polysaccharide is hydroxyethylated to reduce its viscosity and improve the hydration. This material should be readily biodegraded in typical waste treatment plants.

The large number of different types of surfactant materials and the multipurpose functions which they serve makes this particular group of materials extremely difficult to characterize.

The wetting agents and detergents are either nonionic or anionic surfactants. Nonionic types are generally preferred since they do not cause problems by interaction with cationic materials. Ethylene oxide adducts of alkylated phenols and fatty alcohols are products in common use. Anionic products such as fatty amidoethyl sodium sulphonate or sodium salts of sulphated fatty alcohols may also be used occasionally. Structures of products of these types are shown in Appendix B.

A number of materials are also used as leveling agents. The principal products are (1) ethoxylated secondary alcohols, (2) ethoxylated nonylphenol, (3) sodium naphthalene sulphonate, (4) sodium dioctyl sulphosucinate, (5) disodium salt of disulphonated diphenyl oxide, (6) sulphonated castor oil, and (7) sodium salt of phosphated ethoxylated alkylphenol. Structures are shown in Appendix B. Compounds 1, 2, and 7 are used in disperse dyeing of nylon, compounds 4, 5 and 6 are used for dyeing nylon with acid dyes, and compounds 4 and 8 are frequently used in continuous dyeing of nylon [30]. Most of these products are sold as 30 to 75% solutions of the active ingredient in water and/or isopropyl alcohol.

The most commonly used compatibilizers are ethoxylated fatty amines. Ethylene oxide adducts of amides of fatty acids are also probably used as compatibilizers. Compounds classified as leveling agents (2) and (7) are also useful as compatibilizers. Structures are given in Appendix B.

The discovery that silicone type antifoaming agents increase the flammability of carpets has led to the use of large quantities of nonsilicone containing antifoaming agents. These materials are generally 100% active mixtures of mineral oils, 85%, and stearamides (stearic acid amides of ethanol amines), 15%. The vast majority of antifoam agents in current use in the carpet industry are of this type.

A small quantity of silicone based antifoam agents is used in continuous dyeing. These materials contain about 5% of a fluid silicone in water with small quantities of emulsifier.

Softeners, antisoil and antistatic agents are generally cationic type surfactants. Fatty amides are frequently used as softeners with emulsions of low molecular weight polyethylene also frequently used. These materials are designed to exhaust on the fiber and therefore are not discharged in waste water in large volumes. Table 17 also includes estimates of the percent active ingredient present in textile auxiliaries. The values shown are average values based on literature data and analyses of a number of these products in the Georgia Tech laboratories.*

As indicated in Table 17, with few exceptions, dyeing auxiliaries are discharged in the spent dye bath. Many of these compounds are found, therefore, in effluents from carpet processing operations.

Chemical auxiliaries used in printing of carpet are listed in Table 18. The quantities used by companies in the data base are shown in column 2.

* See Appendix C

Table 18

Chemical Auxiliaries Used in Carpet Printing
by Companies in the Data Base and Estimated
Use and Discharge in 1974

Chemical Type	Pounds Used (Data Base)	Factor	Total Industry Use in 1974 (Pounds)	% Active Component	% Exhaustion	Pounds Discharged in 1974 (1000's)
Formic Acid	49,151	55.77	2,741,151	87	0	2,385
Gum Thickener	189,475	55.77	10,567,040	100	0	10,567
Antifoam Agent	86,940	55.77	4,848,644	100	0	4,849
Print Aids	133,548	55.77	7,447,972	100	0	7,448
Wetting Agents	40,981	55.77	2,285,510	50	0	1,143

The factor for estimating the total industry consumption was obtained by dividing the total quantity of nylon carpet printed by the quantity printed in the data base. In general, the auxiliaries used in printing are 100% active and do not remain on the carpet but are removed in the washing step following printing.

The gum thickener used in printing is a modified galactomannan gum obtained from the locust bean tree. The gum is usually modified by carboxymethylation of some of the hydroxy groups. The principal antifoam agents used in printing are 2-ethylhexanol and 2-methylpentanol. This component is sometimes referred to as a screen release agent. The 2-ethylhexanol is used much more frequently than 2-methylpentanol. The print aids used are principally benzyl alcohol. Some small quantities of nonionic surfactants may also be used in print aid formulations. Wetting agents used in printing are generally anionic surfactants of the types previously discussed.

C. Chemicals From Latexing and Backing Processes

In carpet backing operations latex wastes are supposed to be segregated from other wastes. Only very small quantities of chemicals from latexing and backing operations should become a part of the water-bourne wastes. The only exception to this occurs in the foam backing of carpet that is printed. The foam backing is a sulphur cured rubber and a number of chemicals are leached out during the washing of the printed carpet. Based on the compositions given in Table 9, the quantities of chemicals discharged from foam backing of carpet are estimated in Table 19. Industry standards for foam backed carpet suggest a foam weight of 38 ounces per square yard. For a typical printed carpet the face yarn weight is of the order of 11 ounces per square yard. The quantities in column 3 of Table 19 were obtained by multiplying

Table 19

Chemicals Discharged in 1974 From Foam Backing of Carpet

Chemical Type	Pounds Per Pound of Latex	Pounds Per Pound of Face Yarn	Total Pounds Used in 1974 (1000's)	% Discharged	Total Pounds Discharged (1000's)
Rubber Latex	0.2400	.8291	114,524	0	-
PotassiumOleate	.0084	.0290	4,006	90	3,605
Filler	.7199	2.4869	343,515	0	-
Trimene Base	.0024	.0083	1,146	90	1,031
Zinc Diethydithiocarbonate	.0060	.0207	2,859	90	2,606
Zinc Mercaptobenzothiozole	.0024	.0083	1,146	90	1,031
Sulfur	.0036	.0124	1,713	0	-
Zinc Oxide	.0096	.0332	4,586	0	-
Antioxidant	.0036	.0124	1,713	0	-
Potassium Hydroxide	.0005	.0017	235	100	235
Ammonium Acetate	.0036	.0124	1,713	100	1,713

the formulation information in column 2 by 38/11. The total pounds used in 1974 for foam backed, printed carpet (column 4) were then obtained by multiplying column 3 by the total estimated quantity of nylon printed carpet produced in 1974 (138,130,000). The percent discharged in column 5 was estimated from the expected behavior of these compounds in the printing operation. Total estimated discharge in 1974 is given in the last column of Table 19.

In addition to the components shown in Table 19, the rubber latex usually contains surface active agents used in the latex preparation (compounds such as sodium laurel sulfate, di-2-ethylhexylsuccinamide sodium sulfate).

Other compounds from latexing and backing operations should not enter the waste stream except through spillage or failure to properly segregate latex wastes.

D. Summary of Chemical Discharge in 1974

A summary of chemical discharge resulting from piece dyeing of carpet in 1974 is given in Table 20. The data in Table 20 are given in pounds of chemical discharged per 1000 pounds of yarn converted into finished carpet.

Two changes were made in the data of Tables 16 and 18 in the conversion to Table 20. First, the data on dye discharge in 1974 (Table 16) does not account for the fact that changeover in color on continuous dye units and printing units result in at least 10% waste dye liquor and print paste. These wastes are accounted for in quantities of chemical auxiliaries discharged in Table 17, since almost all these auxiliaries are ultimately discharged in spent dye bath and rinse water. However, this loss is not accounted for in the case of dyes due to the high exhaustion indicated in Table 16. The quantities of dyes discharged for dyes used in continuous dyeing and printing have thus been increased by 10% of the quantity consumed in these operations to account for waste involved in style changeovers. The 10% figure is believed to be conservative based on conversations with industry experts. No change was made in quantities of dyes used primarily in beck dyeing. This change increases the discharge of the dyes indicated by an asterisk in Table 16 by a factor of 2.

The second modification is necessary due to a problem in the data base. The data base for carpet printing is somewhat smaller than desired and may therefore overly reflect problems in individual companies. Careful analysis of the data suggests that, at least one company surveyed, had an unusually high print paste waste. This was determined from the quantity of

Table 20

Quantities of Chemicals Discharged in Piece Dyeing of Carpet in 1974

Chemical Type	Total Quantity Discharged in 1974 (1000 pounds)	Quantity in Pounds per 1000 Pounds Face Yarn	Primary Environmental Recepient
Fiber Finish Components			
Lubricant	2,220	1.68	water
Emulsifier	1,776	1.34	water
Antistatic Agent	444	0.34	water
Perservative	4	-	water
Fiber Production By-Products			
Caprolactam	2,947	2.23	water
Polyester & Nylon Oligomers	1,513	1.14	water
Other Fiber Related Chemicals			
Tints	160	0.12	water
Lubricants (Primary Backing)	593	0.45	water
Dyes			
Disperse Yellow 23	25	0.02	water
Acid Yellow 19	22	0.02	water
Acid Yellow 151	4,832	3.66	water
Acid Yellow 135	20	0.02	water
Disperse Yellow 3	17	0.01	water
Disperse Yellow 54	17	0.01	water
Acid Red 151	16	0.01	water
Acid Red 337	14	0.01	water
Disperse Red 60	12	0.01	water
Acid Orange 128	11	0.01	water
Disperse Blue 120	8	0.01	water
Acid Blue 40	6	-	water
Acid Blue 25	5	-	water
Erionyl Orange 3G	5	-	water
Acid Red 266	5	-	water
Disperse Orange 59	5	-	water
Basic Yellow 53	4	-	water
Disperse Yellow 42	3	-	water
Acid Yellow 198	3	-	water
Disperse Blue 7	3	-	water
Disperse Blue 56	3	-	water
Disperse Red 55	3	-	water
Lignin Sulfonate	1,300	0.98	water
Other Diluents (NaCl, Sugar, Na_2SO_4)	2,237	1.69	water

Table 20
(cont.)

Chemical Type	Total Quantity Discharged in 1974 (1000 pounds)	Quanity in Pounds Per 1000 Pounds Face Yarn	Primary Environmental Recepient
pH Control Chemicals			
Monosodium phospate	3,403	2.57	water
Tri-and tetra-sodium phosphate	5,066	3.83	water
Acetic acid	2,117	1.60	water
Formic acid	2,993	2.26	air
Sodium carbonate	529	0.40	water
Ammonium hydroxide	92	0.07	air
Sodium hydroxide, Potassium hydroxide	299	0.23	water
Ammonium Sulfate	924	0.70	water
Diammonium hydrogen phosphate	65	0.05	water
Ammonium acetate	1,746	1.32	water
Carriers			
Biphenyl	4,731	3.57	air
Methyl benzoate	3,548	2.68	air
Naphthalene & Naptha	2,366	1.79	air
Emulsifier (nonionic)	1,183	0.89	water
Auxiliaries			
Antifoaming agents	5,280	3.99	water
Leveling agents	2,137	0.61	water
Wetting Agents, Detergents	5,816	4.39	water
Sequestrants	224	0.17	water
Softeners, Antistatic, Antisoil Agents	48	0.04	water
Compatibilizers	905	0.68	water
2-ethylhexanol	3,637	2.75	water
Benzyl alcohol	5,586	4.22	water
Print and Continuous Dye Gums	10,235	7.73	water
Anifoaming agents, Silicone Type	25	0.02	water
Misc. Chemicals			
Trimene Base	1,031	0.78	water
Zinc Mercaptobenzothiazole	1,031	0.78	water
Zinc Diethyldithiocarbamate	2,606	1.97	water
Sodium and Zinc salts from Scouring Agents	1,767	1.34	water

print gum and other auxiliary chemicals relative to the quantity of carpet printed. To correct for this situation, it appears that the data on quantities of chemicals discharged in printing (Table 19) should be reduced by approximately 25%. This has been done in compiling Table 20.

Finish lubricants shown in Table 20 reflect only the per cent of all face yarn that were piece dyed in 1974.

As noted in the last column of Table 20, most textile processing chemicals are nonvolatile and will be discharged primarily in waste waters from carpet processing plants. The dye carriers and some acids, bases and alcohols are the few exceptions to this general statement.

Chemical structures for the more commonly used textile anxiliaries are given in Appendix B.

The quantities of chemicals discharged per 1000 pounds of face yarn converted to carpet depend on a number of variables. These factors will change with major changes in coloration processes (e.g., decrease in beck dyeing) or with changes in the per cent of the total carpet face yarn which is nylon verses polyester or other fibers. Some of these changes are discussed in Section V.

V. PROJECTED CHEMICAL USAGE IN 1980

Most projections indicate that the carpet industry will process between 2.4 and 2.6 billion pounds of face yarn in 1980 [31]. Nylon is estimated to account for 77-80% of the fiber used for face yarn. The projected techniques for coloration of carpet are shown in Table 21. The major changes predicted (in addition to the increased quantity of carpet produced) is the increase in continuous dyeing and printing relative to beck dyeing. The effect of these changes on the factors used to predict consumption of various

Table 21

Estimated Carpet Coloration by
Different Techniques in 1980

Nylon

Method	Million Pounds	%
Yarn Dyed	245	12
Beck Dyed	300	15
Printed	560	28
Continuous Dyed	895	45
Totals	2000	100

Polyester

Method	Million Pounds	%
Yarn Dyed	20	7
Beck Dyed	160	57
Continuous Dyed	100	36
Totals	280	100

Other Fibers

Method	Million Pounds	%
Yarn Dyed	220	100

All Fibers 2.5 Billion Pounds

dyes and chemical auxiliaries is shown in Table 22. These factors for 1980 can be used to estimate 1980 consumption in the same way that the data base was used to calculate 1974 consumption. Some increase in the data base for continuous dyeing and printing would be diserable for improving the accuracy of the 1980 projected chemical use.

Several technical changes are anticipated which will alter the chemical use pattern between now and 1980. First, due to pressure to reduce phosphates in discharges from carpet mills, increased use of organic acids (acetic and formic acids) and nonphosphate containing salts (ammonium sulfate) is expected. To some extent this trend is already underway and is reflected in the data base for 1974. An even lower phosphate use is expected in 1980.

A second major change in chemical usage will result from development of no carrier dyeing of polyester fiber. All polyester carpet fiber manufacturers are currently working on development of fiber variants which do not require carrier in the dye bath. Success in the development will be difficult but can probably be achieved in the near future. This new fiber variant will have several important consequences - it will make continuous dyeing of polyester more practual, it will increase the per cent of the carpet market of polyester fiber and it will reduce the use of carriers by a significant amount. Carrier usage in 1980 will probably be about 2-5% (by weight) of the polyester fiber processed compared to 7% in 1974. An expected shortage of nylon carpet fiber in the period 1977-1978 may further increase the penetration of polyester in the carpet market [31].

Acrylic fiber manufacturers are also working on a fiber that can be piece dyed in continuous dyeing equipment. Success in this area should

Table 22

Factors Calculated for Estimation
of 1980 Consumption of Dyes
and Auxiliary Chemicals

Fiber and Coloration Process	1974 Factor	1980 Factor
Nylon, Beck Dyeing	10.18	9.48
Nylon, Continuous Dyeing	19.69	63.78
Nylon, Printing	55.77	226.08
Polyester, Beck Dyeing	8.06	9.19

increase the quantity of arcylic fibers processed into carpet with a resulting increase in the use of basic dyes. Due to its higher price, however, acrylic fiber will probably not greatly increase its percentage of the market.

Economic pressures will be a third major factor in changing chemical use patterns. The particular chemicals used in dyeing anxiliaries such as carriers, leveling agents, wetting agents, etc., are extremely sensitive to price. For example, nonionic surfactants have increased significantly in price in the last few years and will probably continue to increase with other petroleum based chemicals. This could lead to partial replacement of these materials by other surfactant types.

A fourth important consideration that must be taken into account is that continuous dyeing and printing are relatively new techniques of carpet coloration. As companies get more experience with these techniques they will discover ways to reduce chemical consumption. A 10% reduction in chemical use in these processes is probably not unreasonable.

Flammability regulations may also alter chemical use somewhat. Changes have already occurred due to the elimination of silicone containing anti-foam agents in carpet dyeing. Since the data base was compiled in the first six months of 1974, retardants are being added to polyester carpet from the dye bath. Approximately 3% tris -2,3 - dibromopropylphosphate is added to the carpet in the dyeing and finishing step. Some of this material will undoubtedly be discharged in carpet mill waste. Other similar additives may be used in the near future.

A fifth factor that will be significant in types of chemicals used will be the introduction of synthetic gums for printing and continuous dyeing.

At the present time modified natural gums are used almost exclusively for this purpose. Work is already underway to develop modified polyacrylic acid gums for these end uses. The new synthetic gums will be less readily biodegraded and could therefore create greater pollution problems than gums currently in use.

Based on fiber consumption alone an increase in chemical use by a factor of approximately 1.9 would be expected by 1980. The increased use of continuous dyeing and printing, with their greater use of chemicals, and the probable savings in chemical use through reduction in carrier dyeing and increased efficiency will probably mean that total chemical use in 1980 will be approximely twice the use in 1974.

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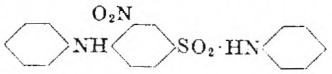
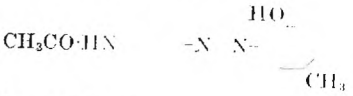
Structures of Some Dyes and Diluents Used in Carpet Coloration

10338 **C.I. Disperse Yellow 42** (Supplément) (*Bright yellow*)



Condense aniline (2 mol.) with 4-chloro-3-nitrobenzenesulfonyl chloride

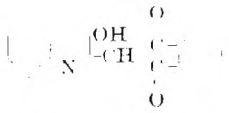
11855 **C.I. Disperse Yellow 3** (*Yellow*)



p-Aminoacetanilide → *p*-Cresol

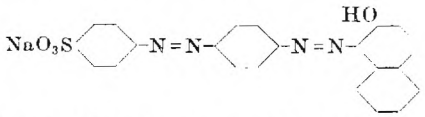
47020★ Disperse Yellow 54

Sulfonated



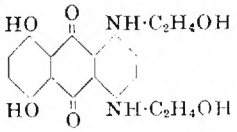
Condense 2-methyl-3-hydroxyquinoline (2-methyl-3-quinolinol) with phthalic anhydride and sulfonate the product

26900 **C.I. Acid Red 151** (*Red*)



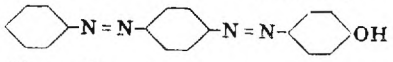
p-(*p*-Aminophenylazo)benzenesulfonic acid → 2-Naphthol

62500 **C.I. Disperse Blue 7** (*Bright greenish blue*)



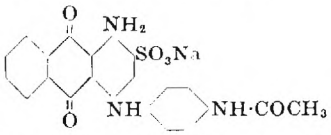
(*a*) Condense leuco-1,4,5,8-tetrahydroxyanthraquinone with ethanolamine in the presence of a little hydrosulfite. Oxidise in the presence of ammonia and boric acid or caustic soda or piperidine
(*b*) Condense leuco-1,4,5,8-tetrahydroxyanthraquinone and ethanolamine in ethanol and oxidise the product

26070 **C.I. Disperse Yellow 23** (*Reddish yellow*)



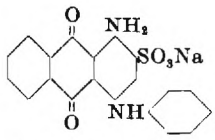
p-Phenylazoaniline → Phenol

62125 **C.I. Acid Blue 40** (*Greenish blue*)



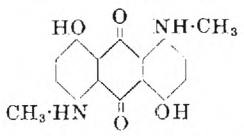
Condense 1-amino-4-bromo-2-anthraquinonesulfonic acid with *p*-aminoacetanilide in presence of copper salts and acid-binding agents and convert to the sodium salt

62055 **C.I. Acid Blue 25** (*Blue*)



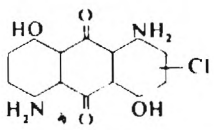
(*a*) Condense 1-amino-2,4-dibromoanthraquinone with aniline and heat the 1-amino-4-anilino-2-bromoanthraquinone so formed with aqueous sodium sulfite in phenol under pressure
(*b*) Condense 1-amino-4-bromo-2-anthraquinonesulfonic acid (Na salt) with aniline in aqueous medium using copper salts as catalyst

63305 **C.I. Disperse Blue 26** (*Bright blue*)



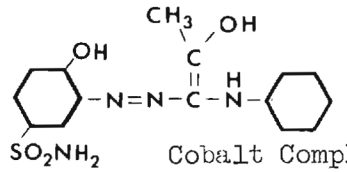
(*a*) Treat 1,5-dihydroxy-4,8-dinitroanthraquinone with methylamine
(*b*) Methylate 1,5-diamino-4,8-dihydroxyanthraquinone with dimethyl sulfate in sulfuric acid

C.I. 63285 **C.I. Disperse Blue 56**



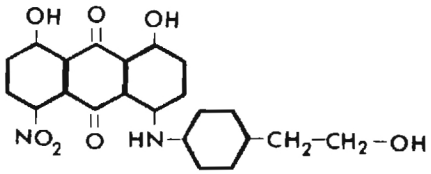
APPENDIX A (Cont.)

13906 C.I. Acid Yellow 151

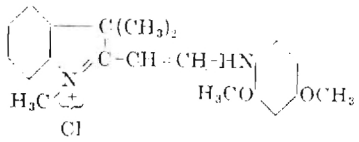


Cobalt Complex

60756 C.I. Disperse Red 60



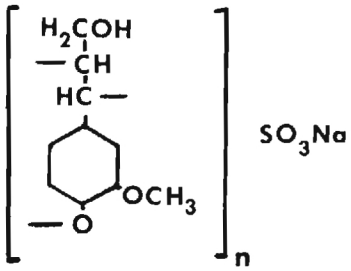
48055 C.I. Basic Yellow 11 (*Bright yellow*)



Condense 1,3,3-trimethyl-1[illegible]-indolineacetaldehyde with 2,4-dimethoxyaniline

COMMON DISPERSANTS AND DILUENTS

Lignin sulfonate (a sulfonated complex polymer of coniferyl alcohol)



Sugar

Sodium chloride

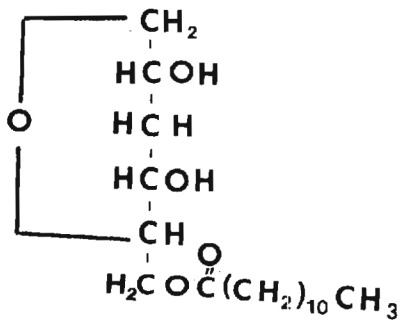
Dextrin

APPENDIX B

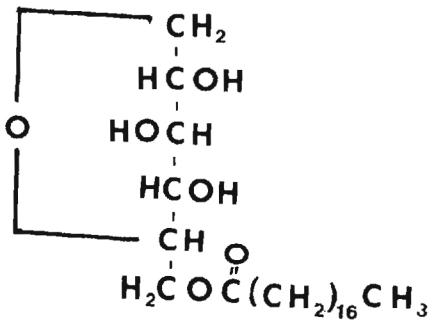
TYPICAL STRUCTURES OF AUXILIARIES AND SURFACE ACTIVE AGENTS USED IN CARPET PROCESSING

FIBER FINISH COMPONENTS

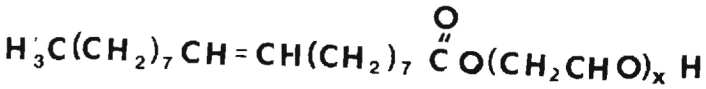
LUBRICANTS



Sorbitan monolaurate

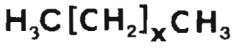


Sorbitan monostearate



Polyethylene glycol oleate

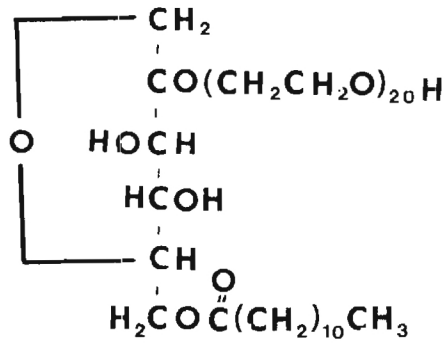
Polyethylene glycol



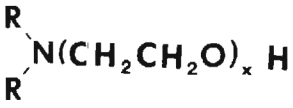
White Mineral Oil

APPENDIX B (Cont.)

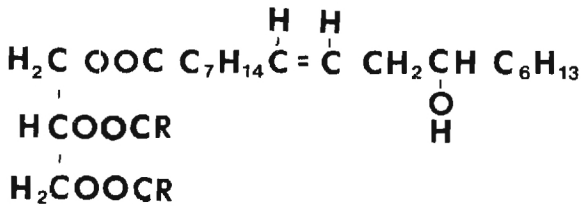
FINISH EMULSIFYING AGENTS



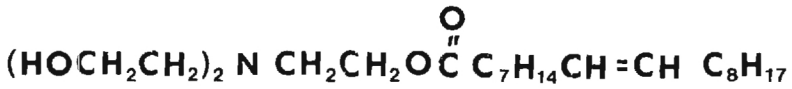
Polyoxyethylenated sorbitan monolaurate



Polyoxyethylenated amines



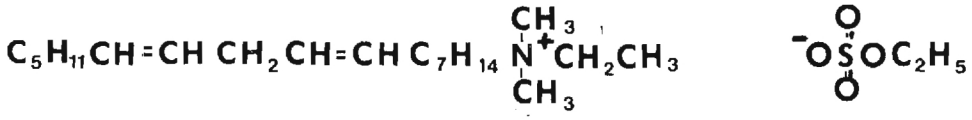
Polyoxyethylenated castor oil



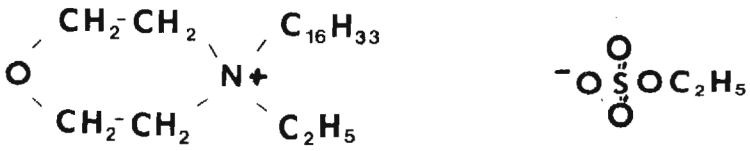
Triethanolamine oleate

APPENDIX B (Cont.)

FINISH ANTISTATIC AGENTS

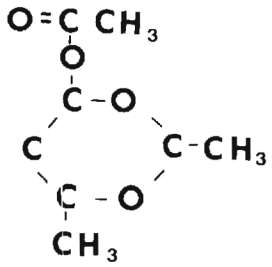


Soya dimethyl ethyl ammonium ethosulfate



N-cetyl N-Ethyl Morpholinium ethosulfate

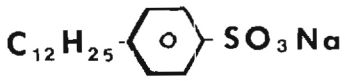
FINISH PERSERVATIVE



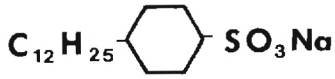
2,4 -dimethyl-6-acetoxy-m-dioxane

APPENDIX B (Cont.)

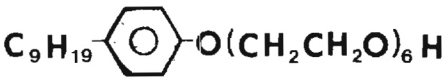
WETTING AGENTS



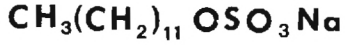
Alkylbenzene sulphonate (ABS)



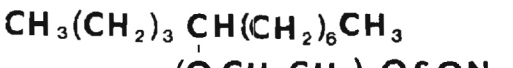
Linear alkylbenzene Sulphonate (LAS)



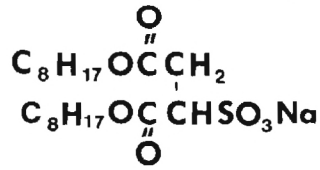
Ethoxylated nonylphenol
(also octylphenol)



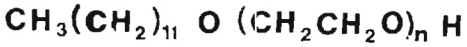
Laurel alcohol sulfated
(also oleyl, stearyl and
other alcohols)



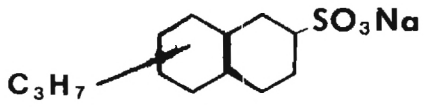
Ethoxylated and sulfated secondary
alcohol



Sodium Dioctyl
Sulphosuccinate



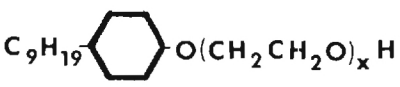
Ethoxylated laurel alcohol (also stearyl, oleyl, and
other alcohols)



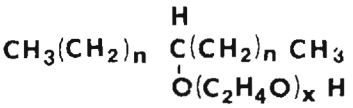
Alkylated naphthalene sulphonate

APPENDIX B (cont.)

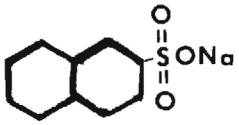
LEVELING AGENTS



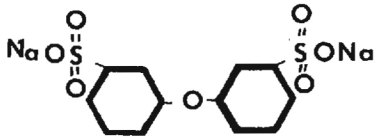
Ethoxylated Nonylphenol



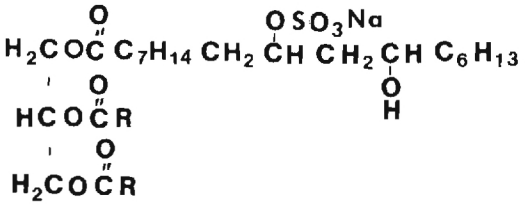
Ethoxylated Secondary Alcohol



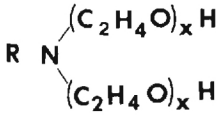
Sodium Naphtalene Sulphonate



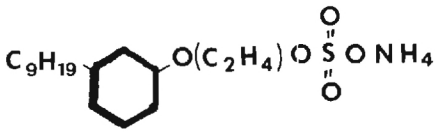
Sodium Salt of Disulphonated Diphenyl Oxide



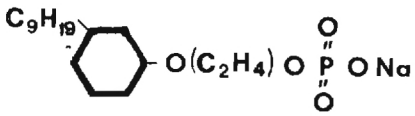
Sulphonated Castor Oil



Ethoxylated Amine

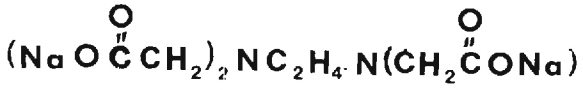


Ammonium Salt of Sulphonated Nonionic

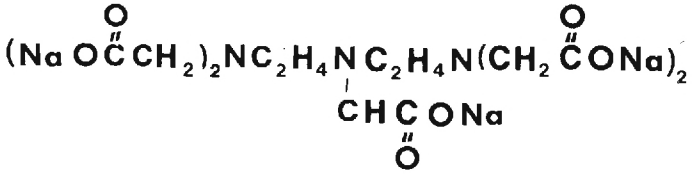


Sodium Salt of Phosphated Nonionic

SEQUESTRANTS



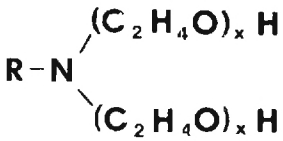
Sodium salt of ehtlenediamine tetracetic acid



Sodium salt of diethylenetriaminepentaacetic acid

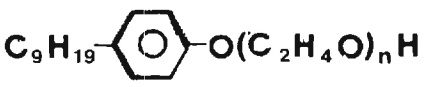
Sodium salt of nitrilotriacetic acid

COMPATIBILIZERS

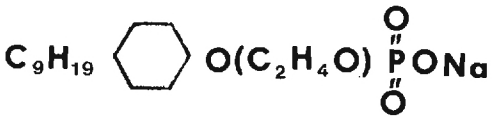


Ethoxylated amine

Ethoxylated fatty acid



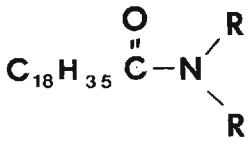
Ethoxylated nonylphenol



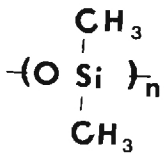
Sodium salt of phosphated ethoxylated nonylphenol

APPENDIX B (Cont.)

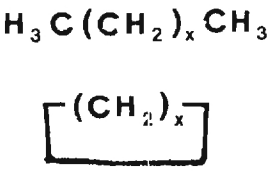
ANTIFOAMING AGENTS



Stearamide

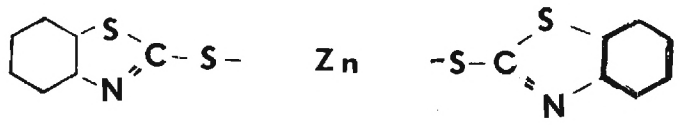


Silicone

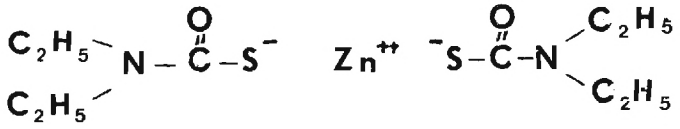


Mineral Oil

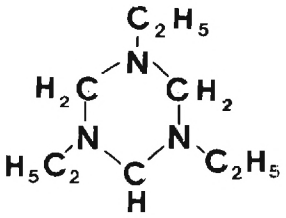
LATEX CHEMICALS



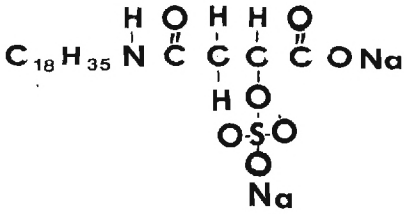
Zinc Mercaptobenzothiazole



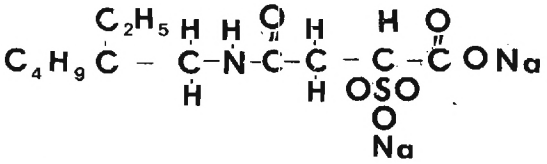
Zinc Diethyldithiocarbamate



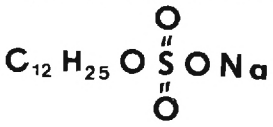
Trimene



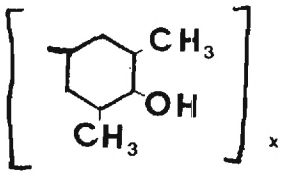
Sulphonated stearyl
succinamide
(foam stabilizer)



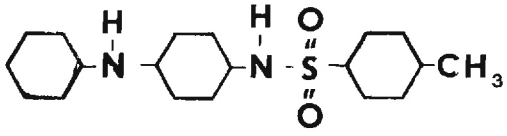
Sulphonated 2 ethylhexyl
succinamide
(surfactant)



laurel sulfate
(foaming agent)



Hindered phenol
antioxidant



P (p-toluene sulfonamide)
diphenylamine
(amine antioxidant)

Appendix C

Experimental Procedures Used in Analysis of Carpet Processing Chemicals

A. Fiber Finish Extractions

The quantity of finish on carpet face yarn was determined by extraction first with cold ether and then with cold chloroform. The extracts were combined, the solvents removed by evaporation, and the residues weighed. Per cent finish was determined by dividing the weight of the residue by the weight of the fiber sample extracted. Results for four different nylon carpet yarn samples are shown below:

Sample	% Finish
1	.65
2	.57
3	.72
4	.55
Average	0.62

Infrared spectra of the extracted material were obtained. Spectra for the various samples were very similiar, the dominant feature being a strong C-O absorption band at 1000 cm^{-1} (probably due to the polyethylene glycol structure). A strong ester carbonyl at 1730 cm^{-1} was also observed. Spectra were very similar to spectra obtained from commercial fiber finishes (Sandoz NP and Spenzit 842).

B. Caprolactum and Cyclic Oligomers in Nylon 6

Approximately 10 gram samples of 3 Nylon 6 carpet yarns were placed in soxhlet extractors and extracted for 5 hours with water. The water was removed in a rotary evaporator and the residues weighed. Results are shown below:

Sample	Sample Weight (g)	Weight of Extract (g)	%
604998	9.735	0.256	2.63
	9.447	0.253	2.68
605096	10.537	0.315	3.00
	9.873	0.326	3.30
60492	9.782	0.320	3.27
	10.013	0.301	3.00

Infrared spectra of the extracts indicated that the extracts were primarily caprolactam and its oligomers with small quantities of fiber finish.

A second sample of 604998 was extracted with cold ether, cold chloroform and finally hot water. The combined extracts were 2.63% by weight, suggesting that the finish, caprolactum, and oligomers were removed in the water extraction. Assuming a finish level of approximately 0.5% (see A above) these samples contained from 2 to 2.5% of extractable caprolactam and its oligomers.

C. Finish Oils on Backing Fabrics

Samples of carpet primary backing fabrics were heated in 250 ml of water at the boil for 1 1/2 hours. The fabrics were removed and the water extract evaporated to dryness in a rotary evaporator and weighted. Weight of the extracts and per cent finish removed are shown below:

Sample	Sample Weight (g)	Weight of Extract (g)	%
Jute	4.02	0.1624	3.99
Woven polypropylene	2.56	0.0533	2.08
Nonwoven polypropylene	2.19	0.0242	1.11

D. Solids Content of Liquid Dyes

Commercial samples of a number of commonly used liquid dyes were obtained from dye manufacturers and evaporated to dryness in a rotary evaporator. Some liquid dyes were dry after 6 hours, others required up to 20 hours to complete removal of water. Results for several liquid dyes

are given below:

Dye	% Solids (by weight)
Acid Blue 25	29
Acid Red 151	40
Acid Orange 128	21
Acid Yellow 135	39
Acid Yellow 151	20

E. Purity of Commercial Disperse Dyes

Commercial disperse dyes commonly used in carpet dyeing were obtained from dye manufacturers. Samples were placed in soxhlet extractors and extracted with benzene for 48 hours. The pure dye was recovered from the extract by evaporation of the benzene. Solutions of known concentrations of the pure dye in dimethylformamide and the commercial dye were prepared and the absorbance determined with a Beckman DB-G spectropbotometer. Plots of absorbance versus concentration for both the pure and commercial dyes were prepared and the per cent purity determined from the ratio of the slopes of the curves

$$\% \text{ purity} = \frac{\text{slope of curve for commercial dye}}{\text{slope of curve for pure dye}}$$

A typical plot is shown in Figure C-1.

Results for several important carpet dyes are given below:

Disperse Yellow 23	19%
Disperse Yellow 54	25%
Disperse Orange 59	31%
Disperse Red 60	16%
Disperse Blue 120	12%

F. Exhaustion Studies

The quantities of dyes remaining in the dyebath at the conclusion of the dye cycle were determined by carrying out laboratory dyeing experiments. Approximately 5 gram samples of nylon carpet were placed in laundrometer

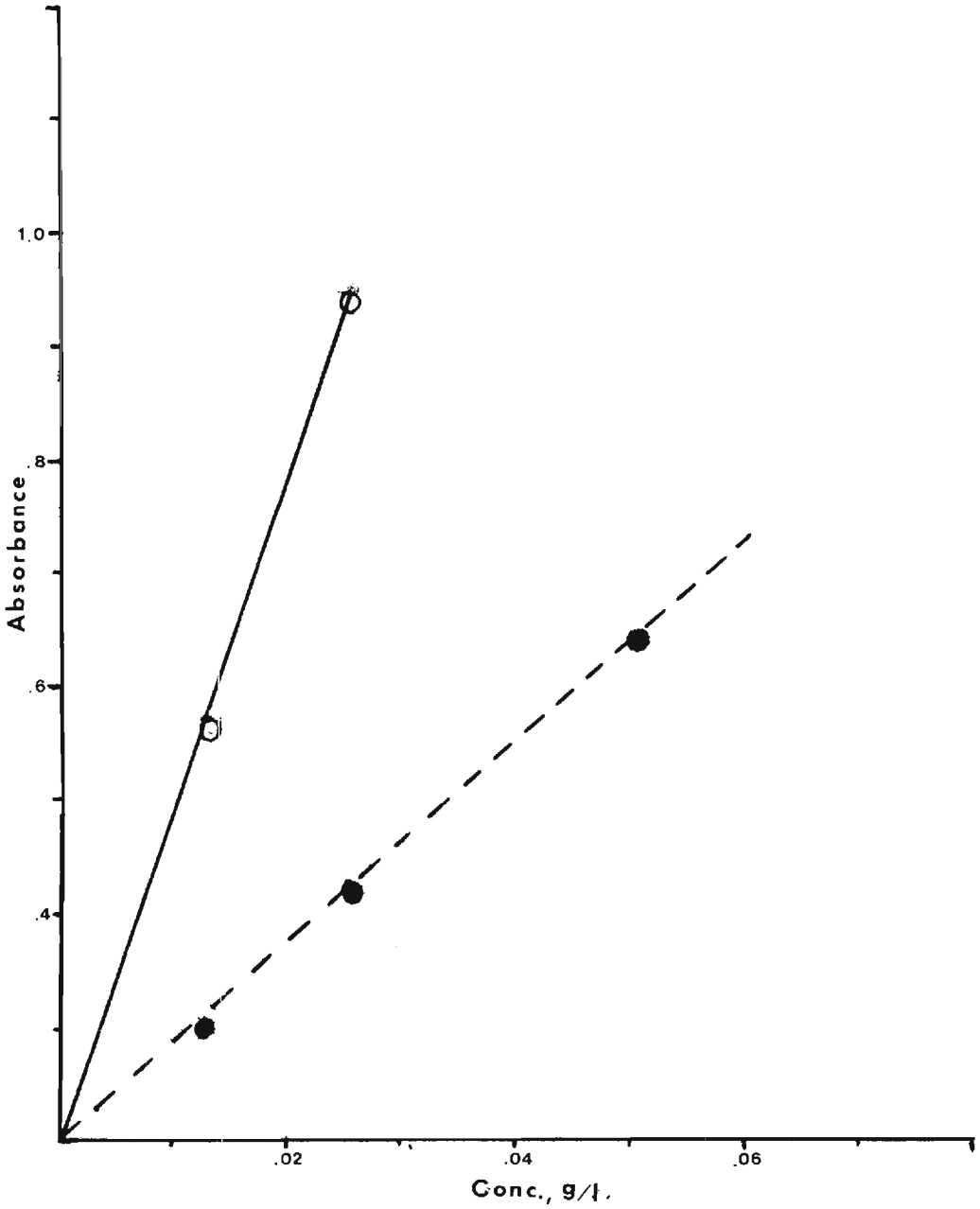


Figure C-1 Absorbance versus concentration for Disperse Orange 59 commercial sample (-●--●-) and pure dye (-○—○-).

cans containing approximately 125 ml (25:1 liquor ratio) of the following dye solution:

disperse dye	1%
wetting agent	0.5%
leveling agent	1.0%
TSP	2.0%
sequestrant	0.5%

The dyebath was heated to 100°C at 2°C/minute and held at 100°C for 1 hour. At the conclusion of the dye cycle the carpet samples were removed and the quantity of dye remaining in the bath determined spectrophotometrically.

A similar procedure was used for disperse dyes on polyester except that 7% of a biphenyl carrier was also added to the dyebath. For dyeing with acid dyes on nylon the bath contained 1% dye, 0.5% leveling agent, 0.5% MSP and 1% sequestrant. Results of the dye exhaustion studies are given on page 41.

G. Active Ingredients in Textile Auxiliaries

The per cent solids of a number of auxiliary chemicals used in carpet processing was determined by placing the commercial samples in a rotary evaporator and removing the volatile components. In those materials investigated the volatile component was either water or a water-isopropyl alcohol mixture. The per cent solids by weight of a selected group of textile auxiliaries is shown below

Auxiliary	% Solids (by weight)
Leveling agent 1	52.3, 54.7
Leveling agent 2	51.0, 47.5
Wetting agent	67.3
Softener 1	52.0
Softener 2	31.9
Sequestrant (concentrated)	65.1, 69.2

G. Analysis of Carriers

Samples of the three most commonly used carriers for polyester carpet dyeing were obtained and analyzed by a number of techniques including gas chromatography, infrared spectroscopy, nuclear magnetic resonance spectroscopy and fluorescence spectroscopy. The gas chromatograms of two of the carriers showed 3 peaks that were shown by mixed injection with pure compounds to be methylbenzoate, napthalene and biphenyl. The per cent of each component was determined by areas under the peaks. The third carrier also contained naphthalene and biphenyl. The third component in this carrier was a mixture of hydrocarbons containing perhaps some chlorinated benzenes. Both the NMR and infrared spectra support these identifications. Results of the carrier analyses are shown below:

Carrier	% Comp. (G.C. detectable*)			
	Pet. dist.	Methyl Benz.	Naphtle.	Biphenyl
#1	-	38	24	38
#2	-	24	19	57
#3	50**		23	27

* 3% SE-30 on Chromasorb W (acid washed) 120°C; 50 ml/min He carrier flow - flame ionization detector

** may contain 5-10% chlorinated benzenes, and definitely xylenes.

Appendix D

Toxicity Data For Carpet Processing Chemicals

Toxicity data for chemicals used in carpet processing are given in Table D-1. These data were obtained from the "Toxic Substances List, 1974 Edition" (U.S. Department of Health Education and Welfare) and a report published by the American Dye Manufacturers Institute entitled "Dyes and the Environment".

Table D-1

Toxicity of Some Common Textile Processing Chemicals

Dyes

Chemical	Species	Route of Administration	Toxicity[+]
Disperse Yellow 3	fathead minnow	oral	TL50: > 180 mg/L
Acid Yellow 151	fathead minnow	oral	TL50: 29 mg/L
Disperse Yellow 54	fathead minnow	oral	TL50: > 180 mg/L
Disperse Red 60	fathead minnow	oral	TL50: > 180 mg/L
Disperse Blue 7	fathead minnow	oral	TL50: 52 mg/L
Acid Blue 25	fathead minnow	oral	TL50: 12 mg/L
Disperse Yellow 42	fathead minnow	oral	TL50: > 180 mg/L
Acid Yellow 38	fathead minnow	oral	TL50: 23 mg/L
Basic Yellow 11	fathead minnow	oral	TL50: 3.2 mg/L

Fiber Finish Components and Residues

Chemical	Species	Route of Administration	Toxicity
Polyethyleneglycol-monosterate	rat	oral	TDLo: 3600 mg/kg
	hamster	-	TDLo: 10g/kg
Polyethylene glycol	dog	intravenous	LDLo: 3000 mg/kg
Mineral oil	mouse	skin	TDLo: 40 gm/kg
Caprolactam	rat	oral	LD50: 2140 mg/kg
	human	inhalation	TDLo: 7ppm

pH Control and Scouring Chemical

Chemical	Species	Route of Administration	Toxicity
Acetic acid	rat	oral	LD50: 3310 mg/kg
Ammonium acetate	human	inhalation	TDLo: 816ppm
Ammonium hydroxide	rat	intravenous	LD50: 98 mg/kg

Table D-1 (Cont.)

pH Control and Scouring Chemical (cont.)

Chemical	Species	Route of Administration	Toxicity
Sodium carbonate	rat	oral	LDL0: 4000 mg/kg
Formic acid	rat	oral	LD50: 1210 mg/kg
Sodium perborate	mouse	intraperitoneal	LD50: 538 mg/kg
Monosodium phosphate	rat	intramuscular	LD50: 250 mg/kg
Potassum hydroxide	rat	oral	LD50: 365 mg/kg
Sodium chloride	rat	oral	LD50: 3000 mg/kg
	human	oral	TDLo: 8200 mg/kg
Sodium hydroxide	rabbit	oral	LDLo: 500 mg/kg
Aluminum sulfate	mouse	intraperitoneal	LD50: 270 mg/kg
Sodium sulfate	rabbit	intravenous	LDL0: 4470 mg/kg

Carrier Components

Chemical	Species	Route of Administration	Toxicity
Biphenyl	rat	oral	LD50: 2180 mg/kg
	rabbit	oral	LD50: 2400 mg/kg
Methyl benzoate	rat	oral	LD50: 1350 mg/kg
Naphtalene	rat	oral	LD50: 1780 mg/kg
Naptha	rat	inhalation	LDL0: 1600ppm
Trichlorobenzene (1,2,4)	rat	oral	LD50: 756 mg/kg
Methylenaphthalene	rat	oral	LD50: 4360 mg/kg

Table D-1 (Cont.)

Surfactants

Chemical	Species	Route of Administration	Toxicity +
Alkylbenzene sulfonate	rat	oral	LD50: 2000 mg/kg
Alkylbenzene sulfonate (linear) Na salt	rat	oral	LD50: 900 mg/kg
Nonylphenol	rat	oral	LD50: 1620 mg/kg
Octylphenol	mouse	intraperitonel	LD50: 25 mg/kg
Ethoxylated octylphenol	mouse	oral	LD50: 3500 mg/kg
Ethoxylated laurel alcohol	mouse	oral	LD50: 3300 mg/kg
Sodium laurel sulfate	rat	oral	LD50: 1288 mg/kg
Naphthalene sulfonic acid	rat	oral	LD50: 400 mg/kg
Ethoxylated amine (C_{12}-C_{18})	rat	oral	LD50: 500 mg/kg
Sodium bis(2-ethylhexyl) sulfosuccinate	mouse	oral	LD50: 4800 mg/kg

Sequestrants

Chemical	Species	Route of Administration	Toxicity +
Na ehtylenediamine nitriloacetic acid	mouse	intraperitoneal	LD50: 330 mg/kg
Trisodium nitrilocetic acid	mouse	intraperitoneal	LD50: 500 mg/kg

Miscellaneous Chemicals

Chemical	Species	Route of Administration	Toxicity +
Zinc mercaptobenzothiazole	rat	oral	LD50: 540 mg/kg
Zinc diethyldithiocarbamate	rat	oral	LD50: 3340 mg/kg
	rabbit	oral	LD50: 570 mg/kg
Benzyl alcohol	rat	oral	LD50: 1230 mg/kg
2-ethyl hexanol	rat	oral	LD50: 800 mg/kg

+ Note: LD50 lethal dose 50 percent kill

TDLo lowest published toxic dose

LDLo lowest published lethal dose

TL50 lethal concentration 50 percent kill

E-27-626

Final Report
Part II

Analysis for Organic Contaminants From Carpet Processing

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Prepared Under Contract No.
E-27-626

for

Environmental Protection Division
Department of Natural Resources
State of Georgia

The preparation of this report was financed in part through a grant from the U.S. Environmental Protection Agency under provisions of Section 106 of the Federal Water Pollution Control Act Amendments of 1972.

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Summary

Pollutants from carpet processing operations may be divided into five major groups from an analytical chemistry perspective. These five groups are inorganic compounds, volatile organic compounds, dyes, surfactants and other nonvolatile organic compounds. Analytical methods are readily available for the first two and a part of the last group. Methods are not readily available for dyes and surfactants.

An analytical procedure for dyes in waste water has been developed based on concentration of the dye on macroreticular resins (Amberlite XAD-2), separation by thin-layer chromatography, and quantitative analysis by visible absorption spectroscopy. Studies with dye solutions of known concentration indicate that the procedure gives better than 80% recovery and detection of the majority of dyes used in carpet processing. Studies on a carpet mill effluent suggest that no major problems are expected in using this procedure with waste water samples.

A fluorescence spectroscopic technique has been developed for determination of aromatic nonionic and anionic surfactants at the parts-per-million level. This technique can also be used with waste water samples and in conjunction with standard procedures for anionic and nonionic surfactants should permit quantitative analyses for four surfactant types (aromatic nonionic, aliphatic nonionic, aromatic anionic, and aliphatic nonionic).

Based on these studies it appears that high pressure liquid chromatography should be on excellent technique for analysis of carpet dyeing wastes.

TABLE OF CONTENTS

I. Introduction

In a previous report on this project [1] a detailed analysis of carpet production processes was presented and the identities and quantities of chemicals used and discharged by the carpet industry were given. The results reported in this previous work were based on data obtained from processing of over 65 million pounds of carpet face yarn in 1974. Information on types and quantities of chemicals used in carpet processing have been used in the present study to guide the development of analytical techniques for carpet processing chemicals in streams carrying carpet industry effluents.

Materials used and discharged by the carpet industry can be divided into 5 major categories. The species in each of these categories and the current status of analytical techniques for these species is reviewed below.

A. Inorganic Compounds

Approximately 13 million pounds of inorganic compounds were discharged in 1974 by the carpet processing industry. Major components were:

Monosodium phosphate	Sodium hydroxide
Trisodium phosphate	Ammonium sulfate
Tetrasodium pyrophosphate	Diammonium hydrogen phosphate
Sodium carbonate	Ammonium acetate
Ammonium hydroxide	Sodium and zinc salts

Analyses for sulfur, phosphorous, sodium , nitrogen, and zinc should provide the necessary data on quantities of these materials present in carpet processing effluents. Analytical techniques for the species are, in general, highly developed and readily available[2]. A combination of atomic absorption and wet analytical techniques should be satisfactory for anlyses for these components.

B. Volatile Organic Components

A number of the organic components of textile wastes are sufficiently volatile to be determined by gas chromatography. Included in this group are:

Acetic acid	Naptha
Formic acid	2-ethylhexanol
Biphenyl	Benzyl alcohol
Methyl benzoate	Mercaptobenzothiazole
Naphthalene	Diethyldithiocarbonate
Caprolactam	Mineral oil
Trimene	2,4-dimethyl-6- acetoxy-m-dioxane
Trichlorobenzene	Monochlorobenzene
Isopropyl alcohol	Dichlorobenzene

An estimated 40 million pounds of these materials were discharged in 1974.

Volatile organic compounds can be detected and quantitated by chromatography or by mass spectroscopy-gas chromotography in combination. These techniques have already been applied to stream samples carrying carpet processing effluents and a number of the volatile organic compounds listed above have been found [2,3]. Other, at present, unidentified peaks in the gas chromatograms of these stream samples may be assigned now that a more comprehensive list of textile processing chemicals is available.

C. Dyes

This group contributed approximately 0.3 million pounds to carpet industry wastes in 1974. Despite the small volume, this group of components is responsible for a number of the adverse effects of carpet processing effluents on water quality. The high color and resistance to biological degradation of dyes create difficult problems in processing textile wastes. The following twelve dyes account for more than 50% of the dye discharged by the carpet industry.

Disperse Yellow 23	Acid Red 151
Acid Yellow 19	Acid Red 337
Acid Yellow 151	Disperse Red 60
Acid Yellow 135	Acid Orange 128
Disperse Yellow 3	Disperse Blue 120
Disperse Yellow 54	Acid Blue 40

Techniques for analysis for dyes in waste water have received little attention in the literature. This area was selected therefore for study in the current research efforts and the results are given in Section II.

D. Surfactants

This large class of textile processing chemicals accounts for approximately 16 million pounds of carpet waste. The group includes many different classes of surfactant materials. A list of the primary components and their classification (see Reference 5) is

given below:

Class IA.1.1	Ethylene oxide adducts of caster oil
Class IA1.4	Ethylene oxide adducts of fatty acids
Class IA2.2	Ethylene oxide adducts of phenols (nonyl, octyl)
Class IA2.3	Ethylene oxide adducts of fatty alchols
Class IA1.3	Ethylene oxide adducts of fatty acid esters of Sorbitan
Class IA1.7	Fatty acid esters of Sorbitan
Class IB1	Metal salts of fatty acids
Class IIB1.1.1	Metal salts of sulfated castor oil
Class IIB1.3.2	Metal salts of sulfated ethylene oxide adducts of phenols
Class IIB1.5	Metal salts of sulfated fatty alchols
Class IIB2.1.3	Metal salt of sulfonated lignin
Class IIB2.2.3	Metal salts of esters of short chain sulfocarboxylic acid
Class IIB2.5	Metal salts of sulfonated naphthalenes
Class IIIA1.1.2	Monoethanolamide of fatty acids
Class IIIA6.1	Ethylene oxide adducts of fatty amines
Class IIIA10.1	Tetralkyl ammonium salts of fatty acids
Class VB2.1	Metal salts of phosphated ethylene oxide adducts of phenols

This list includes, anionic, cationic and ampholytic type surfactants. Fatty acids used in production include C-10 (capric), C-12 (lauric), C-14 (myristic), C-16 (palmitic), and C-18 (stearic, oleic, linoleic, linolenic) carbon chains.

Analytical techniques are available for anionic surfactants as a group. These tests generally depend on development of color in solution containing these surfactants and the intensity of color formation can be used for quantitation. A number of color forming reagents are available for anionic surfactants. Procedures are not available for determination of nonionic surfactants at the parts-per-million level. Techniques for analyses of these materials have received considerable attention in the present work. These techniques are discussed in Section III.

E. Other Nonvolatile Organic Components

Several other organic compounds are present in carpet processing effluents. The principal materials are

polyester oligomers	1.5 million pounds
sequestrants	0.2 million pounds
gums	10.2 million pounds

Procedures are available for sequestants but procedures for the other components in this group are not available.

II. ANALYTICAL PROCEDURES FOR DYES IN CARPET WASTE

Based on the previous studies of chemical use in the carpet industry [1], it was estimated that dyes would be present in carpet processing waste at the fractional parts-per-million level. Analytical techniques for dyes (visible absorption spectroscopy) can readily detect dyes at the parts-per-million level. A 10 to 100-fold concentration procedure was therefore necessary to obtain dyes at a

concentration suitable for quantitative analysis. Since dyes always occur in mixtures in waste water, a separation procedure was also required.

The most distinctive characteristic of dyes is their very strong absorption of energy in the visible region of the spectrum. This characteristic was selected for development of quantitative analytical methods for various dyes of interest. A typical working curve of absorbance versus concentration for one of the dyes in this study (Acid Red 167) is shown in Figure 1.

Two major classes of dyes - acid dyes and disperse dyes - and a few basic dyes are used for carpet piece dyeing. Fifteen dyes from these classes were selected for study and are shown in Table 1.

A. Concentration Procedures

The necessity for up to a 100-fold reduction in volume of waste water to concentrate dye waste suggested that some type of adsorption procedure would be most convent for the concentration step. Two adsorption methods have been investigated in some detail for removing organic compounds from waste water - carbon adsorption [6-8] and adsorption on macroreticular resins [9-12]. Removal of acid and basic dyes from water was very good (>80%) by both of these materials but removal of disperse dyes was poor. Development of concentration procedures based on adsorption, therefore, required that some means be found to improve the efficiency of disperse dye adsorption.

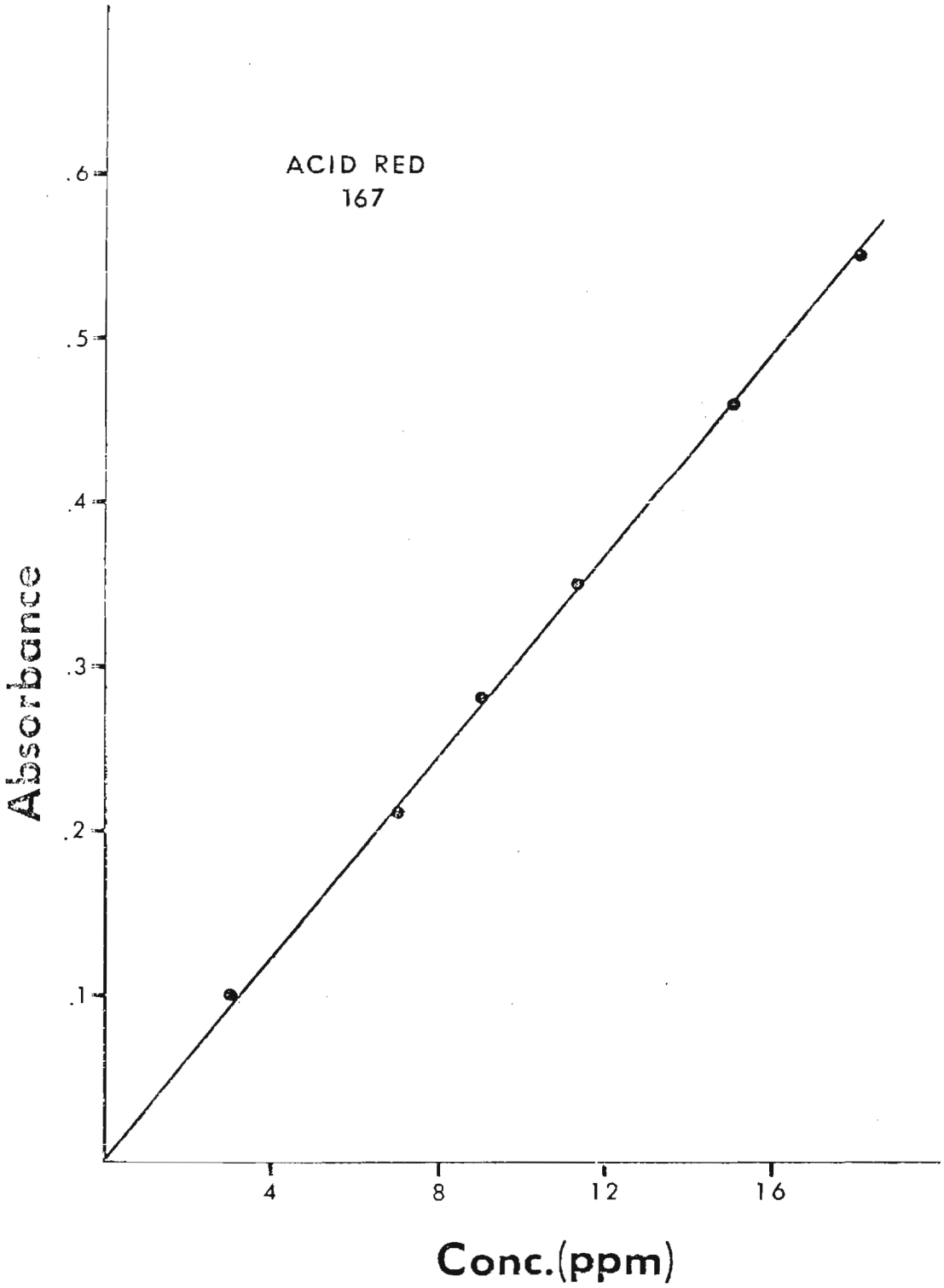


Figure 1--Analytical working curve for Acid Red 167.

Table 1

Dyes Selected for Development of Analytical Techniques

Acid Yellow 19	Disperse Blue 7
Acid Yellow 135	Disperse Blue 120
Acid Yellow 151	Disperse Yellow 3
Acid Orange 128	Disperse Yellow 23
Acid Red 151	Disperse Yellow 54
Acid Red 167	Disperse Yellow 55
Acid Red 337	Disperse Red 60
Acid Blue 40	

Disperse dyes, unlike acid and basic dyes are very insoluble in water. Disperse dyes do not actually dissolve in water but exist as aggregates dispersed in the water. Since adsorption is a molecular pehonomena, it was reasoned that some means for producing true solution of disperse dyes in water would dramatically increase the adsorption on carbon or macroreticular resins. Dimethylformamide (DMF) is a good solvent for many disperse dyes and is miscible with water so experiments were conducted on adsorption of disperse dyes from DMF-water solutions. Preliminary experiments showed that the adsorption of disperse dyes were dramatically increased by addition of 90% DMF to the dye in water dispersion. Subsequent adsorption work was therefore conducted on 10% DMF-90% water solutions.

Adsorption on activated carbon was investigated initially. Approximately 15 grams of Nuchar 8 x 30 mesh granular active carbon was placed in a 50 ml burette in a 10% DMF-90% water solution. The column was rinsed several times with the solvent to remove air pockets. The following dye solutions were then passed through the column

31 ml	Acid Red 151	19.20 ppm
30 ml	Acid Red 167	18.04 ppm
30 ml	Acid Yellow 19	20.64 ppm
31 ml	Acid Yellow 38	17.46 ppm
30 ml	Disperse Yellow 54	16.80 ppm
17 ml	Disperse Blue 7	19.52 ppm
50 ml	Disperse Yellow 3	17.41 ppm

After four passes through the column under gravity flow the solutions were colorless. Quantitative measurements on some of the dye solutions after passing through the column gave the data shown in Table 2. It is apparant from these data that greater than 80% removal effeciences for disperse dyes can be achieved by activated carbon from DMF-water solutions.

Difficulties were encountered in trying to remove dyes from the carbon column. A number of techniques were attempted including passing solvents through the column, and sohxlet extraction with solvents. In no instance could more than a few percent of the dye be removed from the column. This approach was abandoned, therefore, as a technique for concentration of dyes.

Experiments were conducted next on adsorption of dyes by macroreticular resins. Some of these resins are copolymers of styrene with divinylbenzene with a high surface-to-volume ratio. Other types are modified acrylate esters. The resins used in this study were obtained from the Rohm and Haas Company and included Amberlite XAD-2, XAD-4, and XAD-7. Preliminary experiments on adsorption of dyes from 10% DMF - 90% water solutions indicated that XAD-2 was the best resin for this purpose. All subsequent experiments were conducted with XAD-2 resin.

The resin columns were prepared as follows:

A chromatography column (9mmID x 500mm, LAB CREST FITTINGS from VWR Scientific) was plugged at one end with glass wool. A Teflon stopcock fitting was attached to the plugged end and the column partially filled with water. A weighed amount (23g) of resin (20-50

Table 2

Dye Adsorption on Activated Carbon

Disperse Blue 7		Disperse Yellow 54	
Original solution	19.52 ppm	Original Solution	18.26 ppm
Solution after adsorption	0 ppm	Solution after adsorption	3.0 ppm
% removed	100	% removed	83.5

Disperse Yellow 3

Original solution	17.41 ppm
Solution after adsorption	0 ppm
% removed	100

mesh used as received from Rohm & Haas, Philadelphia, PA) was added a portion at a time and allowed to partially settle between additions. Excess water was drained from the column as necessary. When the column was full, the open end was plugged with prewetted glass wool and a second column attached. At least one inch of liquid was maintained above the resin in all the following operations.

In order to remove inorganic impurities the resin bed (35 ml vol.) was washed (at ~ 16 bed vols./hr.) with 150 ml of distilled water. In the same manner, organic impurities were removed with 200 ml of methanol. The methanol and air now in the column were removed by backwashing (upflow) with 500 ml of distilled water. A small amount of "fines" were also removed in this step.

Approximately 2 liters of dye solutions of know concentration in DMF 10%-water 90% were passed through the column at a flow rate of 8 to 10 bed volumes (350-450 ml) per hour. The column was washed with approximately 600 ml of distilled water (at 10 bed volumes per hour) to remove residual DMF. The column was then inverted and washed with 4 bed volumes (180 ml) of benzene at 8 to 10 bed volumes (350-450 ml) per hour. Disperse dyes are removed by the benzene. The benzene extraction is followed by 4 bed volumes (180 ml) of methanol and 4 bed volumes of dimethylformamide Acid dyes are removed by the methanol. Dyes removed by the benzene and methanol may be further concentrated by evaporation of the solvent in a rotary evaporater.

Analysis of the dye concentrations in methanol and benzene were obtained by visible adsorption spectroscopy using working curves similar to those shown in Figure 1. The percent of the dye removed from the DMF-water solution and recovered from the column by the methanol and benzene elution are shown in Table 3. Some difficulties were encountered with Disperse Blue 7 due to diffculty in obtaining clear solutions for the spectral analysis. Acid yellow 19 also created problems in that, unlike other acid dyes, this dye was removed from the column by all three solvents (methanol, benzene, DMF). The low value for Disperse Yellow 54 is not consistent with the observed color of the solutions and may be an experimental error.

In general, concentration of the dyes using XAD-2 resin columns appears to be a satisfactory technique for use in analysis for carpet dyes in waste water. An increase in concentration by a factor of 100 can be readily achieved with greater than 80% for the majority of the dyes tested. Even greater recoveries would probably be possible using mixed resin beds with a polar component to more efficiently remove acid dyes. This possibility has not yet been investigated.

B. Separation of Dye Mixtures

A technique for separation of dyes in a mixture was the second requirement in development of an analytical procedure for dyes in carpet processing wastes. Thin layer chromatography has been successfully used for dye separations for a number of years and was the method selected for this study.

Table 3

Dye Concentration (and Recovery)
by XAD-2 Resin

Dye	% Removal and Recovery
Disperse Yellow 3	99
Disperse Yellow 54	57
Disperse Yellow 23	84
Disperse Red 55	85
Disperse Red 60	93
Disperse Blue 7	-
Acid Yellow 38	100
Acid Red 151	100
Acid Red 167	85
Acid Yellow 19	-

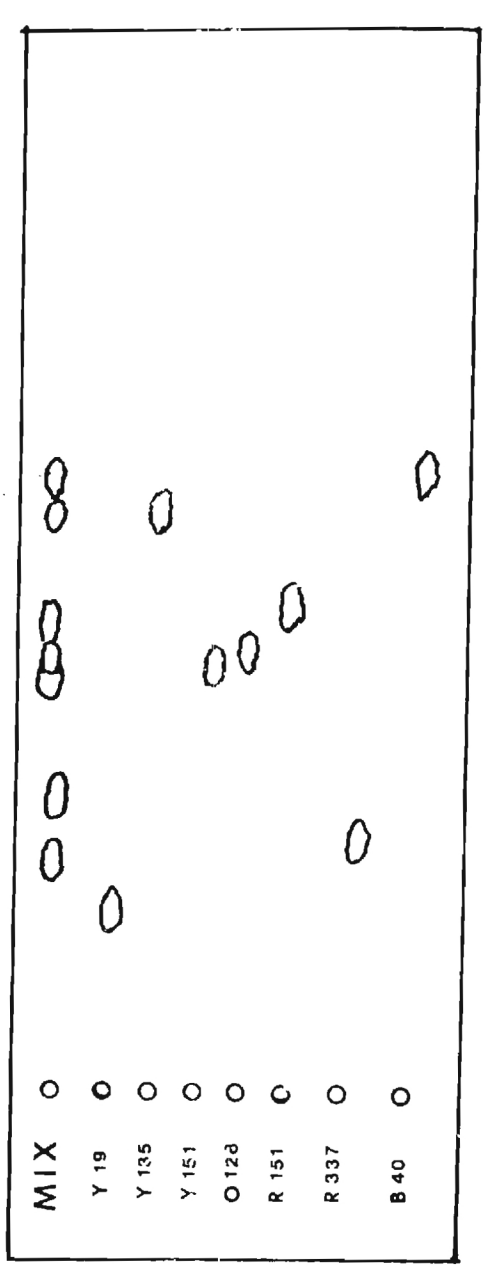
Concentrated solutions of the dyes in benzene or methanol were spotted on Eastman Chromatogram sheets (#13179) precoated with silica gel without fluorescent indicator. Plates with the disperse dyes were developed using a 25% dioxane - 75% carbon tetrachloride solvent system. Two developments with the solvent system gave good separation of a mixture of the seven most commonly used disperse dyes. A drawing of the developed plate is shown in Figure 2.

Plates spotted with seven important acid dyes were developed using a 75% chloroform - 25% ethanol solvent mixture. Results of two developments with this system are also shown in Figure 2. Although separations were not quite as good as for disperse dyes, the results were adequate for quantitation as described below.

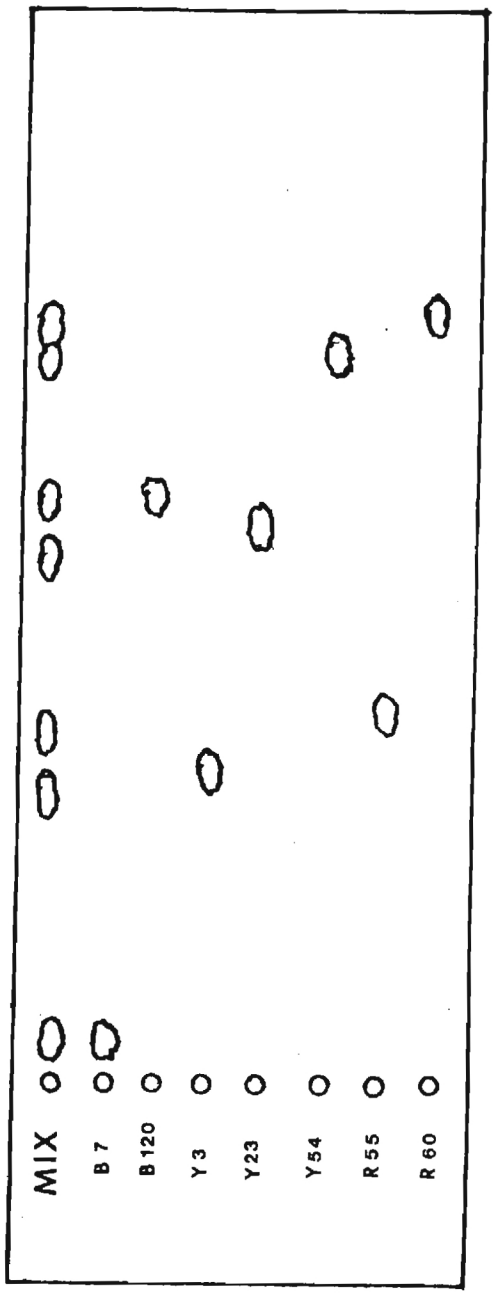
C. Quantitation of Dyes

Quantitative analysis for dyes separated by thin layer chromatography was obtained by cutting the spots from the plates and eluting with a small quantity of methanol (acid dyes) or benzene (disperse dyes). Absorption in the visible region of the spectrum was obtained by placing the dye solution in a 1 cm cell.

Due to their strong absorption in the visible region of the spectrum, analyses for dyes can be readily carried out with few interferences by standard spectroscopic techniques. Quantitative analysis for dyes separated by thin layer chromatography was obtained by cutting the separated spots from the chromatographic plates and eluting the dye with a small quantity of methanol (acid dyes) or benzene (disperse dyes).



ACID DYES



DISPERSE DYES

Figure 2 -- Separation of Acid and Disperse Dyes by Thin Layer Chromatography

Spectra of the solutions were obtained in 1 cm cells with a Beckman DB-G Spectrophotometer. The quantities of the various dyes present were then determined by comparison of the spectra with standard calibration curves (similar to Figure 1).

Quantitative analyses for dyes by this procedure does not require complete separation of all the components of a mixture by the thin layer chromatography technique. For example, Disperse Yellow 54 and Disperse Red 60 and are not completely separated as shown in Figure 2. However, since these dyes have very different absorption spectra, the absorbance at two wavelengths for which the dyes differ significantly in their absorption can be determined and the quantaties of each dye present determined from solution of the two simultaneous equations

$$A_{\lambda 1} = a_{11}c_1 + a_{12}c_2$$

$$A_{\lambda 1} = a_{12}c_1 + a_{22}c_2$$

Where $A_{\lambda 1}$ is the total absorbance at wavelenth 1, $A_{\lambda 2}$ is the total absorbance at wavelength 2, a_{11} is the absorbance of dye 2 at wavelength 1, a_{12} the absorbance of dye 1 at wavelength 2, a_{12} the absorbance of dye 2 at wavelength 2, and C_1 and C_2 are the concentration of two dyes. In theory this technique could be used for mixtures of a large number of dyes, but practically it is limited to no more than 3 or 4 and they must differ in their visible absorption spectra (i.e. two yellow or two blues in a mixture could not be analyzed but two or three dyes of different color can).

D. Test of the Dye Analysis System

In order to determine if the dye analysis system would function satisfactorily with complex textile processing wastes, 20 gallons of effluent from a carpet dyeing plant were obtained and analyzed. The waste contained a quantity of suspended solids which had to be removed by filtration prior to the XAD-2 resin concentration step.

Two liters of the filtrate were passed through the resin column as previously described. Dyes were removed from the resin in benzene and methanol and spotted on thin layer chromatorgraphy plates. Development of the benzene extract gave clear evidence of the presence of Disperse Yellow 23, Disperse Yellow 54 and Disperse Blue 120. This observation was consistant with the fact that polyester carpet was being dyed at the time waste samples were collected.

This experiment confirms that the dye analysis system can be used for complex carpet dyeing wastes.

III. ANALYTICAL PROCEDURES FOR SURFACTANTS

The number and diversity of surfactants used in carpet processing presents a formidable analytical problem. No attempt has been made in this study to analyze for individual surfactants. However, development of techniques for surfactant groups has been attempted. The four major types of surfactants used in carpet processing are aromatic nonionics (ethylene oxide adducts of phenols), aliphatic nonionics (ethylene oxide adducts of alcohols), aromatic anionics (naphthalene sulfonates), and aliphatic anionics (sulfated alcohols).

A. Anionic and Nonionic Surfactants

A survey of analytical methods for surfactants and a number of preliminary laboratory experiments suggest, that for nonionic type materials, colorimetric determination with Dragendorff's reagent would be the technique of choice [5]. This technique is sensitive at the fractional parts-per-million level with nonionics containing at least 5 moles of ethylene oxide and can be adapted to materials with 2 - 10 moles of ethylene oxide. A detailed procedure for this technique is given in the Appendix. The phosphotungstic acid colorimetric method also shows promise for nonionic surfactants.

For anionic surfactants various modifications of the methylene blue test have been used. A more recent colorimetric procedure using triphenyl tetrazolium chloride will be investigated for anionic surfactants [5]. This procedure is also given in the Appendix.

B. Aromatic and Aliphatic Surfactants

In previous work on streams carrying carpet processing wastes [13] it was discovered that a complex fluorescence spectrum was obtained from cyclohexane extracts of the water samples. An example of the fluorescence spectrum from a water sample from the Coosa River is shown in Figure 3. Three separate fluorescent species could be detected in this spectrum-one emitting at approximately 300 nanometers, one emitting at 310 nanometers, and one at approximately 350 nanometers. In the previous work the peak at 310 nanometers was shown to be due to biphenyl but the

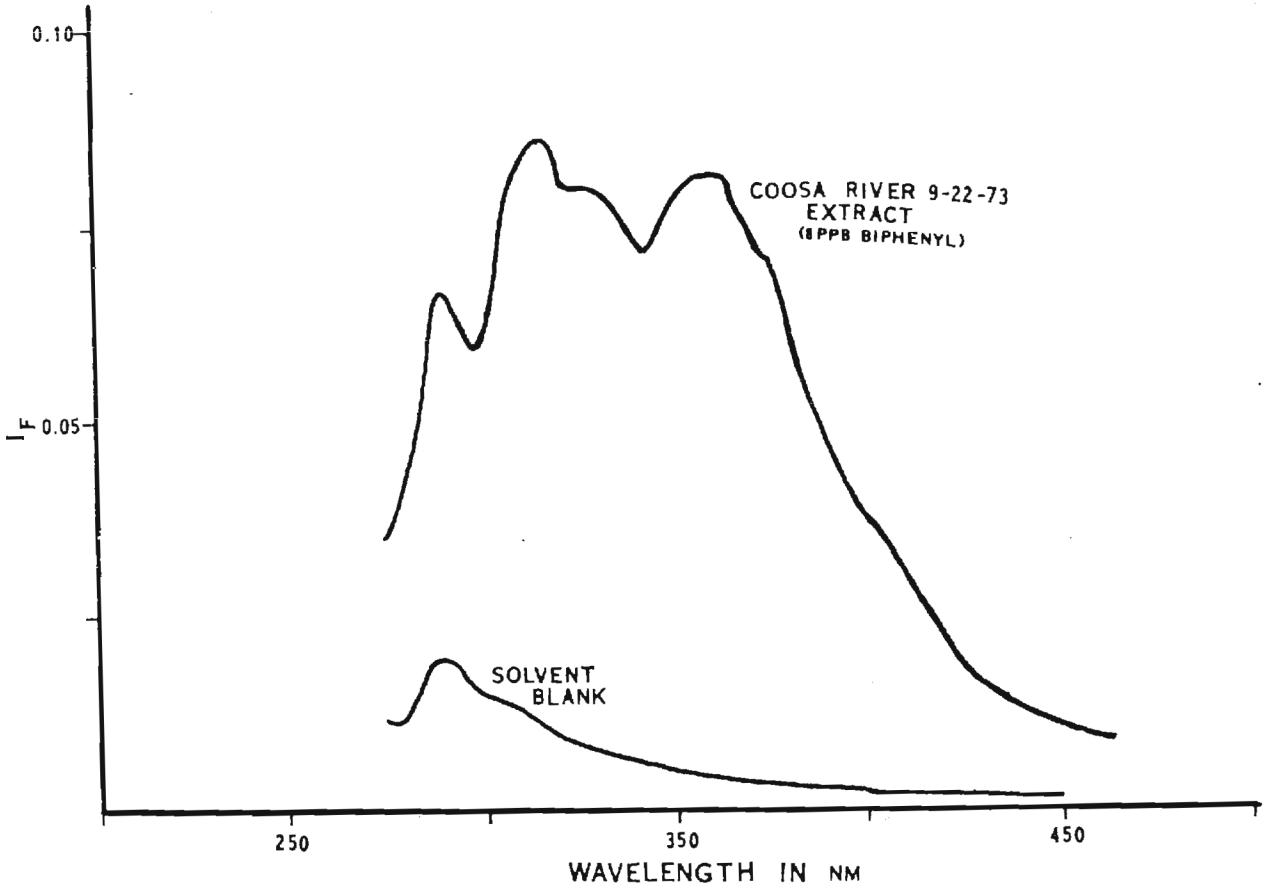


FIGURE 3 -- Fluorescence spectra of cyclohexane and a Coosa River extract (9/22/73).

other fluorescent speices were not identified.

During the course of the current project the fluorescence spectra of a large number of textile processing chemicals were obtained the two previously unknown contaminants have been identified. The peak at 300 nanometers is obtained when nonyl or octyl phenol and their ethylene oxide adducts are excited by radiation at 275 nanometers. The peak at 350 nanometers results from excitation of naphthalene sulfonate or lignin sulfonate at 290 nanometers. Subsequent study of the fluorescence spectra of these compounds suggest that they may be determined quantitatively at the fractional parts-per-million level by this technique. Polyethylene oxides and ethylene oxide adducts of aliphatic compounds do not fluoresce so the technique is specific for aromatic surfactants and their degradation products.

C. Concentration of Surfactants

Using the anlytical techniques described above, the concentration and recovery of surfactants using XAD-2 resins has been studied. A 6.11 part-per-million solution of Igepal CO-630 (nonylphenol with 9 moles of ethylene oxide) in DMF 5% - water 95% was passed through an XAD-2 column at 8 bed volumes per hour. Fluorescence spectra of the effluent showed less thatn 0.5 parts-per-million of Igepal CO-630. Subsequent washing of the column with benzene and methanol and examination of the fluorescence spectra of the extracts revealed that >95% of the original surfactant was in the methanol wash. Thus, concentration of nonionic detergents on an XAD-2 resin column appears feasible.

Similar experiments with an aromatic anionic detergent were also conducted. A 5.20 part-per-million solution of Tanol SN (a naphthalene sulfonate) was prepared in 5% DMF-95% water solvent. The solution was passed through the XAD-2 column at 7.5 bed volumes per hour. Fluorscence examination of the effluent showed that greater than 90% of the Tancl SW came through the column with the solvent. Clearly, XAD-2 will not be effective in concentrating anionic surfactants. It may be necessary to analyze for these materials directly in the waste water of to use an ionic resin bed to concentrate these materials.

One important observation made during these studies was that benzene and methanol remove fluorescent material from XAD-2 columns. These impurities must be removed by prewashing the column with all solvents to be used subsequently in removing absorbed species. The prewash effluents should be checked by fluorescence to ensure that all impurities have been removed.

D. Status of Surfactant Analytical Methods

With the available techniques, it appears that four types of commonly used surfactants can be determined quantitatively.

1. aromatic nonionics
2. aromatic anionics
3. aliphate nonionics
4. aliphatic anioncs

Surfactant types 1 and 2 can be determined spectrofluorimetrically and types 3 and 4 can be obtained by subtraction of the quantities of types

1 and 2 from the total quantities of nonionics and anionics present. Further differentiation and quantitation of surfactant species appears very difficult at the present time.

IV. NEW TECHNIQUES

Recent developments in technology have made rapid and quantitative separation of complex mixtures possible by high pressure liquid chromatography. In this technique, components to be separated are dissolved in a suitable solvent and pumped into a small column containing a small particle, high surface area adsorbant. The differing partition of the various components between the stationary phase and the moving solvent phase results in a separation of the components as they move down the column. The instrument may be operated in a variety of modes depending on the nature of the stationary phase. In the case of small particle silica columns, a type of adsorption chromatography is responsible for the separation. In other cases a liquid-like hydrocarbon (e.g. C_{18} chains) are absorbed on or bonded to the column and a type of liquid partition is achieved. In other cases ionic species are bonded to the column for separation of polar components. Columns containing specific pore sizes are also available to obtain separations based on molecular size (exclusion chromatograph). This range in operation mode combined with the variety of solvents and solvent mixtures which may be used as mobile phases provides an extremely versatile separation tool.

Detection of components existing from the column is usually achieved by absorption in the UV and/or visible spectrum. Thus, the detector

systems are especially sensitive to dye molecules and the aromatic portions of many surfactant molecules. Other detectors are available (fluorescence, refractive index) and can be used in series with up to 4 detectors operating simultaneously.

Liquid chromatography appears to have great promise for the types of separations discussed in this report. An assessment of the capabilities of this technique in analyses for organic contaminants in streams carrying carpet processing waste should be given high priority.

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Procedure 5.29: **Gravimetric and Colorimetric Determinations with Dragendorff's Reagent (Potassium Tetraiodo Bismuth(III)ate)** (Buerger, 1963C, 1964)

I. *Gravimetric*

Reagents

$BaCl_2$ solution. Twenty grams $BaCl_2 \cdot 2\ H_2O$ in 100 ml solution.

Dragendorff reagent. Dissolve 1.7 g of bismuth subnitrate ($BiONO_3 \cdot H_2O$) in 20 ml of glacial acetic acid, dilute to 100 ml with water. Dissolve separately 40 g KI in 100 ml H_2O. Combine the solutions in a 1-liter volumetric flask, add 200 ml acetic acid, and make up to 1 liter with water.

Combined reagent. Mix 100 ml Dragendorff reagent with 50 ml of $BaCl_2$ solution. The combined reagents keep about two weeks in a brown bottle. Discard when the color has turned brown.

Acetic acid, glacial.

Centrifuge tube, 110 mm long, consisting of an upper portion, 66 mm long and 15 mm i.d., tapering 10 mm to a tube 1 mm wide and 34 mm long.

Procedure

To a 6 ml sample containing 0.1–10 p.p.m polyoxyethylene derivative, add 6 ml combined $BaCl_2$–Dragendorff reagent. After 5 min, a red precipitate forms which is separated by centrifuging in the capillary tube at 3000 r.p.m., estimating the amount of precipitate from its height in the tube.

Sensitivity

0.05 p.p.m. nonionic. Effective with adducts containing $\geq$ 5 mole ethylene oxide.

Discussion

To determine nonionics and their polyglycol impurities separately (Buerger, 1963B), the aqueous nonionic solution is repeatedly extracted with methyl ethyl ketone (1:1). The ketone phase is evaporated and the residue is redissolved in water. This separates polyglycols, which remain in the aqueous phase. The reagent is added to either or both of the extracts.

The method is adaptable to polyoxyethylene derivatives with 2–10 moles of ethylene oxide/mole by using aqueous isopropyl alcohol as the solvent (Buerger, 1964) and freshly prepared reagent.

Buerger states that this method is suitable for fatty acid-, fatty alcohol-, lower alcohol-, fatty amine-, fatty acid amide-, alkylphenol-, and polyoxypropylene-derived polyoxyalkylenated compounds down to the range of pentaethylene glycol or pentapropylene glycol.

Cationic or anionic surfactants, proteins, and protein hydrolyzates do not give the reaction. Polyoxyethylenated anionics or cationics do, however.

II. *Colorimetric: Bismuth as Pyrrolidine Dithiocarbamate*

Wickbold (1966) redissolves the Dragendorff reagent–nonionic complex (centrifuged and washed with glacial acetic acid) with 3 ml of ammonium tartrate (12.4 g tartaric acid and 17.6 ml NH_4OH, to 1 liter). The resulting solution is reacted with pyrrolidine dithiocarbamate in a medium of 350 ml H_2O, diluted to 1 liter with acetone). Absorbance of the yellow bismuth complex formed is measured at 405 mμ and compared with a calibration curve. By using larger samples and concentrating the nonionic by means of repeated extraction with butanol before the addition of the reagent, very small quantities of nonionic can be determined. The pyrrolidine dithiocarbamate reagent was recently described by Kali (1968). It is available as K + K Labs. (Plainview, N. Y.) reagent #2081.

Tests for Anionic Surfactants

Test 2.12: Thymol Blue Test (Peter, 1954)

Reagent

Five milliliters of 0.005 *N* hydrochloric acid solution containing 3 drops of 0.1% thymol blue.

Procedure

To 5 ml neutral (0.01–0.1%) surfactant solution, add 5 ml reagent. A reddish purple color indicates anionic surfactant.

Test 2.13: Test for Anionic Sulf(on)ates (Renault, 1960)

Reagents

1. Triphenyl tetrazolium chloride, 1% solution, freshly made (TPT).
2. Buffer, pH 2.5; dissolve 7.5 g aminoacetic acid and 5.8 g NaCl in 1000 ml dilute HCl.
3. Dibromoethane
4. Cetyl trimethylammonium bromide, 0.5% aqueous.
5. 1% $Na_2S_2O_4$ (sodium dithionite) in pH 7 phosphate buffer.

Procedure

To 40 ml test solution (in which excess acid or alkali have been neutralized as needed by dropwise addition of HCl or NaOH), add 10 ml pH 2.5 buffer and 1 ml fresh 1% TPT reagent. Extract twice with 5-ml portions of $C_2H_4Br_2$. Separate the solvent phase, wash it three times with 10-ml portions of buffer diluted 1:2 with water, dry the organic phase with Na_2SO_4, and to the clear solution add 2 ml of the cetyl trimethylammonium bromide solution and three drops of the dithionite solution. If a pink to red color develops, anionic sulf(on)ate is present.

Sensitivity. The test detects 1–5 p.p.m. of anionics, such as sulfated primary and secondary alcohols, sulfated polyhydric alcohol fatty acid esters, sulfated polyoxyethylene derivatives of fatty alcohols or phenols, sulforicinoleates, and alkyl sulfonates or alkylbenzenesulfonates.